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TRANSLATED FROM RUSSIAN

TO THE MEMORY OF ACADEMICIAN NIKOLAI DMITRIEVICH ZELINSKY

The death occurred on July 31, 1953, at the age of ninety-two of the eminent chemist Academician Nikolai Dmitrievich Zelinsky, senior professor at the M.V. Lomonosov Moscow State University, Hero of Socialist Labor, recipient of three Stalin prizes, and holder of four Orders of Lenin and two orders of the Red Banner of Labor. In the person of Zelinsky Soviet science has lost a great organic chemist, founder of the science of heterogeneous organic catalysis and of petroleum chemistry, inventor of the first universal charcoal gas mask in the world, scientist of manifold activities, and teacher and trainer of several generations of chemists.

Zelinsky was the author of about six hundred original scientific papers and inventions in the fields of organic, physical, and inorganic chemistry, including petroleum chemistry and the chemistry of artificial liquid fuel. The investigations of Zelinsky and his school, the largest in the USSR on the synthesis of hydrocarbons, organic catalysis, petroleum chemistry, and protein chemistry, have occupied and continue to occupy a leading position in world science.

N. D. Zelinsky was born on February 6 (New Style), 1861, in Tiraspol in the province of Kherson (now Moldavian Autonomous SSR). At the age of two he lost his father, and a year and a half later his mother died also. He was brought up by his maternal grandmother, M. P. Vasilyeva, a good, sympathetic, cultured woman, very progressive in ideas for the time in which she lived; Zelinsky retained fond memories of her to the last days of his life. He received his early education from his grandmother, and she provided for his further education at the Rishelyevsky Gymnasium in Odessa, which he attended until 1880. While still a schoolboy, Zelinsky listened enthusiastically to the lectures of the eminent physiologist I. M. Sechenov at the university. From the gymnasium, Zelinsky passed to the Natural History Department of the Physico-mathematical Faculty of the Novorossiisky University (Odessa), which he attended until 1884. His first chemistry teachers at the university were F.F. Klimenko, A. A. Verigo, V. M. Petriev, and P. G. Melikov (Melikishvili). It was under the direction of Melikov that Zelinsky, as a student, carried out his first scientific investigation on the "Product of the Addition to Methylamine to β-Methylglycidic Acid", which was published in 1884 in the Journal of the Russian Physicochemical Society.

With regard to his first teacher, P. G. Melikov, Zelinsky wrote with great warmth of feeling in 1950: "All my life I have been constantly grateful to my teacher for the attention and cooperation that he gave to me over a period of many years"; and also "The memory of this man, who was my first teacher, I preserve as the best of my memories of my student days at the Novorossiisky University".

In biology Zelinsky's teachers included the eminent Russian scientists A. O. Kovalevsky (zoology), I. I. Mechnikov (embriology and evolutionary theory), and L. S. Tsenkovsky (botany).

Personal intercourse and friendship with his eminent teachers, and later with the giants of Russian progressive science — I. M. Sechenov, K. A. Timiryazev, P. N. Lebedev, N. A. Umov, and A. G. Stoletov — had an exceptional favorable influence on the formation of the materialistic world-view of N. D. Zelinsky, whose interests in the future were to range over such a wide field of science, and who as a research chemist was to enter into the highest ranks of the creators of world chemical science.

Soon after completing his course at the Novorossiisky University, Zelinsky was sent as a faculty stipendiary to Germany, where he worked under the great organic chemists of that time, J. Wislicenus (Leipzig) and Prof. Victor Meyer (Göttingen), and then somewhat later, during his second visit abroad, under the famous Wilhelm Ostwald, one of the founders, after Lomonosov, of classical physical chemistry.

The investigational work carried out by the young Zelinsky under the direction of these great chemists determined, to a great extent, the three important directions of his subsequent investigations. He began some

...vestigations, of great interest from the point of view of theory, on the chemical nature and isomerism of compounds of the thiophene series and on the stereoisomerism of carboxylic acids, and these subsequently provided valuable material for his Master's (1889) and Doctor's (1891) theses. In Ostwald's laboratory Zelinsky began his original investigations in physical chemistry and electrochemistry, and these had an important influence on his subsequent classical investigations in organic chemistry and heterogeneous catalysis.

It is worthy of note that Zelinsky, the future inventor of the charcoal gas mask, while carrying out the synthesis of the then unknown tetrahydrothiophene in Victor Meyer's laboratory at Göttingen, obtained mustard gas, i.e. bis (2-chloroethyl) sulfide, for the first time, and, not suspecting the toxicity of the intermediate product in his synthesis, became the first victim of this treacherous, poisonous substance; he had to remain in the hospital for a whole term with badly burned arms.

On returning to Odessa, Zelinsky immediately began to build up his investigational school, bringing together his first students and collaborators, among whom we may note A. A. Bychikhin (later professor at the Novorossiisky University), A. M. Bezredka (later deputy director of the Pasteur Institute in Paris), S. G. Krapivin (later second professor at Moscow State University), and A. G. Doroshevsky (later first privatdocent at Moscow State University). In the Odessa period of his activities the main attention of Zelinsky and his students was concentrated on the synthesis of many di- and tri- substituted succinic, glutaric, adipic, and pimelic acids, and also of some substituted dibasic hydroxy acids, and the investigation of the stereoisomerism phenomena exhibited by these substances. Stereochemistry was then a completely new branch of organic chemistry, and here in Russia Zelinsky was one of the first bold investigators and exponents in this fruitful field of ideas. Zelinsky's investigations on isomerism in the thiophene series and the stereoisomerism of dibasic aliphatic acids made a substantial contribution to the development of A. M. Butlerov's Theory of Chemical Structure, the secure materialistic basis of organic chemistry.

On the recommendation of D. I. Mendeleev, N. D. Zelinsky was invited in the summer of 1893 to take up the post of extraordinary professor at Moscow University in the department of analytical and organic chemistry, and from that time, and for the remainder of his life (nearly sixty years), Zelinsky carried out exceptionally valuable scientific, pedagogic, administrative, and social work within the walls of the university, as well as in the Academy of Sciences of the USSR, to which he was elected as Active Member in 1929.

In Moscow University, Zelinsky's attention gradually passed over to a new, wide, and very important field, the chemistry of alicyclic hydrocarbons, or naphthenes. Before this time remarkable investigations had been made in Russia in this direction by such eminent chemists as F. R. Wreden, F. F. Beilstein, D. I. Mendeleev, and V. V. Markovnikov. Zelinsky, however, in this field also made a path for himself, bridging over from the dibasic carboxylic acids of the aliphatic series that he had studied so thoroughly to the alicyclic systems. This bridging over was possible because of the perfection and further development by Zelinsky of Wislicenus' cycloketonization of dibasic carboxylic acids.

In the period from 1834 to 1911 Zelinsky with his students and coworkers synthesized and characterized more than forty hydrocarbons of the cyclopentane and cyclohexane series. Many of them, and many of those synthesized later in the detailed investigations made by Zelinsky into the chemical nature of Soviet Petroleum, have served as valuable standards in the establishing of the composition of narrow gasoline fractions. It should be noted that also in this new field of work much attention was given to the stereochemical side of the study of cyclic hydrocarbons.

The following investigations belong to this first period of Zelinsky's activities at Moscow University: the remarkable work on the pyrogenetic decomposition of petroleum; the beginning of the classical investigations on selective dehydrogenational catalysis, which was discovered by Zelinsky; the development of a simple method for the preparation of α-amino acids and their esters; the beginning of extensive investigations on the catalytic hydrolysis of proteins and a series of original physicochemical investigations.

N. D. Zelinsky, appreciating the high value of work by A. A. Letny on the pyrolysis of petroleum which had remained unnoticed, made a deeper study of the thermal decomposition of petroleum distillates, and by his direct participation in large-scale trials rendered great scientific and practical service in the development of the pyrolysis industry in Russia. Already in 1901 Zelinsky gave his support to the technologist Nikiforov and helped the latter to realize his project of petroleum pyrolysis at high pressure, as he was engaged in a study of the thermal decomposition of petroleum, he joined with Nikiforov in developing the first variant of the modern thermal cracking of petroleum products.

The field of Zelinsky's investigations on heterogeneous organic catalysis is so wide, and the results are so important and varied in character that we must confine ourselves to a citation of a few of the most brilliant ex-

amples, in which Zelinsky's creative talents are most clearly manifest. Thus, already in 1905, Zelinsky with his
student I. Pappe effected for the first time the conversion of a cyclopentane ring into a cyclohexane ring by contact
catalysis, the example investigated being the conversion of ethylcyclopentane into methylcyclohexane and toluene
in presence of aluminum bromide and bromine. Later, in Zelinsky's laboratories in Moscow State University and
the Academy of Science of the USSR, on the basis of this important discovery, the equilibrium reaction of enlarge-
ment of a five-membered ring was considerably improved by the use of aluminum chloride and determination
of the optimum conditions. It was established by the detailed investigations of Zelinsky and his
students that the content of cyclohexanes in petroleum distillates could be increased by 15–25% with the aid of
this reaction.

In 1911 N D. Zelinsky discovered the now well-known selective catalytic dehydrogenation of cyclohexanes
and their functional derivatives in presence of platinum or palladium black at 300°. This remarkable reaction re-
ceived further study in the later investigations of Zelinsky, working with numerous students and co-workers. In his
work with G. S. Pavlov and A. A. Balandin, the kinetics of dehydrogenational catalysis were studied, and this sub-
ject was developed in detail in later investigations of A. A. Balandin, working with A. M. Rubinshtein, N. I. Shui-
kin, and Yu. K. Yuryev. Mainly on the basis of this extensive material, A. A. Balandin has created his well known
multiplet theory of dehydrogenational catalysis.

To the same year, 1911, belongs the discovery made by N. D. Zelinsky and N. I. Glinka of the very inter-
esting reaction of hydrogen redistribution in cyclohexenes and cyclohexadienes under the catalytic action of finely
dispersed palladium or platinum, in which the corresponding cyclohexanes and aromatic hydrocarbons are formed.
This conversion of labile forms to stable forms is irreversible, and for this reason Zelinsky described the phenomenon
that he had discovered as irreversible catalysis. Later, these investigations were continued by Zelinsky in con-
junction with B. A. Kazansky and R. Ya. Levina, and they developed the irreversible catalysis of hydrocarbons along
lines peculiar to this phenomenon.

In this period Zelinsky's school grew rapidly, always exhibiting exceptional concern for the growth and train-
ing of research teams. The names of the many talented students of N D. Zelinsky speak for themselves; they in-
cluded the well-known chemists A. N. Reformatsky, V. V. Rudevich, N. A. Shilov, L. A. Chugaev, A. G. Generozov,
S. N. Naumov, N. A. Roz anov, L. A. Tselikov, D. K. Aleksandrov, I. F. Gutt, S. S. Nametkin, A. F. Mozer, F. F.
Lebedev, V. V. Chelintsev, E. S. Przhevalsky, A. V. Rakovsky, A. N. Lebedev, G. L. Stadnikov, N. A. Izgaryshev,
N. A. Shlezinger, A. Gorsky, I. V. Fulikov, A. I. Annenkov, A. E. Uspensky, V. P. Kravets, E. M. Berkengeim, V. V.
Longinov, N. L. Glinka, and N. I. Chervyakov. Many of them have occupied and continue to occupy important
positions in the universities and have, in their turn, created their own original directions in science and their own
schools of talented students. Some of Zelinsky's students, such as L. A. Chugaev and N. A. Shilov, who later be-
came eminent scientists and took up high university appointments, in addition to their research work performed
also the duties of lecture assistants to their teacher in talented fashion.

In 1911, in connection with the intensified repression by the Tsarist government of progressive university
teachers and students, N D. Zelinsky decided to leave Moscow University. By a decree issued by one of the most
reactionary satraps of the Imperial government, the Minister of Education L. A. Kasso, the whole presidium of
Moscow University, which consisted of the progressive professors A. A. Manuilov, M. A. Menzbir, and P. A. Mina-
kov, was dismissed. As a sign of protest Zelinsky and a large group of professors and teachers resigned. He then
moved to St. Petersburg, where he took up the post of director of the Central Laboratory of the Ministry of Finances
and head of the commercial department in the Economics Faculty of the Polytechnical Institute.

In St. Petersburg, Zelinsky, in spite of his bitter experiences in connection with leaving the most important
chair in the oldest university in Russia and becoming separated from his large team of students, resumed his
scientific investigations with his former vigor and persistence. It was at this period that he carried out his ex-
tensive and original investigations in conjunction with V. S. Sadikov on the hydrolysis of proteins under press-
ure and began his work on the condensation of acetylene to benzene and its homologs in presence of active char-
coal; in particular it was at this period that he made his unforgettable investigations on the properties of active
charcoal and its use as a universal means of protection from toxic substances. Here also we must mention
Zelinsky's remarkable investigations on the cracking of petroleum hydrocarbons in the presence of natural (al-
uminosilicates) and synthetic oxide catalysts, which thus anticipated Houdry's invention by more than 20 years.
Already in 1915, Zelinsky, on the basis of laboratory and pilot-plant experiments, pointed out, for the first time
in the history of petroleum science, the effectiveness of aluminosilicates and oxide catalysts in the cracking of
hydrocarbons.

During the first world war Zelinsky extended his investigations on the catalytic cracking and pyrolysis of
petroleum distillates, and he helped in the creation of a Russian toluene industry. Guided by his theoretical con-

cepts and experimental investigations and moved by feelings of deep patriotism and love of the Fatherland, N. D. Zelinsky, at the height of the first world war, invented the first universal charcoal gas mask in the world; it saved the lives of hundreds of thousands of Russian soldiers on the battlefield.

In the spring of 1915, as soon as the news arrived of the despicable use by the Kaiser's armies of poison gas against the French, and later the Russian, armies. Zelinsky temporarily abandoned all his other investigations and, with his characteristic energy and zeal, set about developing a reliable means of protection. The idea of using active charcoal for the absorption of poisonous substances (chlorine, phosgene, mustard gas, etc.) arose as the result of his thorough experimental investigations on the absorption of gases and vapors by highly porous substances.

After thorough trials on himself personally, with the participation of his faithful laboratory assistant S. S. Stepanov (who worked hand in hand with him for a total of fifty years), and after the delays that were inevitable at that time in Prince Oldenburg's department. Zelinsky's gas absorber fitted to a rubber mask designed by the engineer Kumant received the warm approval of the High Command, and was adopted in February 1916 for the equipment of the Russian Army.

In his work on the devising of the gas mask, Zelinsky received valuable help not only from Stepanov and Kumant, but also from his colleague Prof. V. S. Sadikov. With justifiable pride, in discussing the gas mask, Zelinsky said, "I invented it not for attack, but for the protection of young lives from suffering and death".

In 1917, shortly after the overthrow of the autocracy, Zelinsky found it possible to return to his chair in Moscow University. After the victory of the Great October Socialist Revolution, Zelinsky's second Moscow period of scientific teaching, and social activities began, and it continued to the end of his long, full, exemplary life. This brilliant period, which lasted more than one-third of a century, was the most fruitful of all —so full of brilliant investigations that it is quite impossible to treat them in a short memorial sketch.

The Communist Party of the Soviet Union and the Soviet government, with the scientific giants Lenin and Stalin at their head, have created all the necessary conditions for the blossoming forth of true science, having paid special attention to the requirements of scientific workers. And under these conditions the remarkable talent of N. D. Zelinsky has developed in its full strength. In unison with the varied manifestations of the majestic creative forces of the highly gifted Russian people, which are directed toward the creation of a bright future for the whole of humanity.

Having resumed his scientific and teaching activities at Moscow State University with particular vigor, N. D. Zelinsky did not interrupt them even at the most difficult periods of the civil war and Anglo-American intervention. Along with him, in the cold half-illuminated laboratories, his faithful assistant S. S. Stepanov and the first students of his second Moscow period, B. A. Kazansky and B. V. Maksorov, worked unselfishly, and they were soon joined by a new group of students of the revivified Moscow State University, including among many others, A. N. Nesmeyanov, K. A. Kocheshkov, M. I. Ushakov, and G. S. Pavlov.

When the interventionists seized the Caucasian oil fields and Soviet aviation was deprived of gasoline supplies, Zelinsky, on the basis of his researches on the cracking of hydrocarbons in presence of aluminum chloride, proposed, and quickly realized in practice, a new method of manufacturing gasoline from the large stocks of petroleum residues and solar oil that were then to be found in the central provinces. This method for the manufacture of aviation fuel rendered extremely valuable service to the young heroic Red Army. Again N. D. Zelinsky showed himself to be a fervent patriot of his now already socialist Fatherland. Shortly after this, by his work on the pyrolytic preparation of benzene from petroleum, Zelinsky made a valuable contribution to the synthetic dye industry that was then coming into being in our country.

It is natural that Zelinsky first of all resumed his long-standing investigations on the catalytic transformations of hydrocarbons and on petroleum chemistry, developing these in close association with his further work on the synthesis of more complex cycloalkanes. In addition to difficultly accessible monocyclic hydrocarbons, Zelinsky synthesized and carefully characterized many interesting bi- and tri- cyclic substances, and also condensed systems.

Zelinsky continued to devote much attention to the synthesis and heterogeneous - catalysis reactions of little known hydrocarbons having spiran structures, which are very interesting from the stereochemical point of view. Together with N I Shuikin and N. V. Elagina, he synthesized a number of spiroalkanes and made a detailed study of their properties and reactions under various conditions. Together with A. E. Uspensky, K. A. Kocheshkov, M. I. Ushakov, B. A. Kazansky, and A. F. Plate, he synthesized difficultly accessible bridged bicyclic systems.

With great persistence and thoroughness, Zelinsky, with the aid of numerous students and coworkers, investigated the chemical nature and composition of gasoline distillates from the petroleums of almost all the important

oil fields of the USSR, particularly the Caucasian fields. By detailed and careful work he determined the nature of the various heterogeneous catalysis reactions of the cyclic hydrocarbons occurring in the gasoline – ligroin fractions, developed new methods for the catalytic treatment of petroleum, and obtained new material in confirmation of the theory of the organic origin of petroleum.

In their work on the catalytic dehydrogenation of gasoline fractions, N. D. Zelinsky and N. I. Shuikin already in 1932 made the extremely important observation that aromatic hydrocarbons are formed in presence of a nickelized alumina catalyst at somewhat above 300° not only as a result of the smooth dehydrogenation of cyclohexanes, but also at the expense of hydrocarbons of other classes. Together with B. A. Kazansky and A. F. Plate in 1934, Zelinsky discovered the very interesting reaction of the opening of a five-membered cycle by means of hydrogen in presence of platinized charcoal at 300 – 310°, i.e. the hydrogenolysis of a five-membered alicyclic system in which there was practically no strain.

In the same year N. D. Zelinsky and N. I. Shuikin proved experimentally for the first time the existence of free methylene radicals under the conditions of methane elimination from cyclohexane in contact with a nickelized alumina catalyst at 330 – 350°. It was thus shown that free radicals can arise by the breakdown of an organic substance in presence of a highly active catalyst, even at such comparatively low temperatures as 300 – 350°.

Together with a team of students and coworkers, Zelinsky has developed, and introduced into industrial practice, an original method for the preparation of toluene and high-quality aviation fuels from petroleum on the basis of further improvements in the dehydrogenation catalysis method that he discovered. In the course of the development of this new Soviet process the scientific principles on which the theory and practice of the use of highly active and stable metal catalysts of the platinum group are based have been greatly extended. All that has been recently brought into wide use in the USA under the name of the platforming process, which has been loudly proclaimed as the achievement of American scientists (V. Haensel and others), was begun and completed in the traditional investigations of N. D. Zelinsky and his school.

Several years before the first "sensational" American publications in 1949, this process, under the name of GRB (the initials of words meaning "deep reforming of gasoline"), was developed by N. D. Zelinsky's students in the Institute of Organic Chemistry of the USSR Academy of Sciences, use being made of alumina and aluminosilicate catalysts containing small amounts of platinum, and also of oxide catalysts containing palladium and nickel.

As he attached great importance to the use of modern physical methods by research chemists, N. D. Zelinsky, together with Academicians B. A. Kazansky and G. S. Landsberg, introduced the combination light-scattering method (i.e. Raman method – Publisher) for the detailed investigation of gasolines, and this, in conjunction with dehydrogenational-catalysis, chromatographic adsorption, and precise rectification, gave valuable scientific and practical results in the quantitative analysis of hydrocarbon mixtures.

We cannot leave the excellent investigations of N. D. Zelinsky on hydrogenational-catalysis without mention: he developed methods for the vapor phase hydrogenation under normal pressure not only of ethylenic bonds, but also of the more stable bonds in benzene, pyridine, and pyrrole nuclei. He used finely dispersed palladium and platinum deposited on active charcoal or asbestos, and so proved the incorrectness of P. Sabatier's assertion that platinum and palladium are unsuitable for hydrogenations in a continuous flow system. Zelinsky discovered still another catalyst of the platinum group having notable hydrogenation properties, namely osmium; he was the first to effect, with the aid of finely dispersed osmium, the delicate reaction of the smooth hydrogenation of the furan nucleus. He carried out the vapor-phase hydrogenation of 2-methylfuran (sylvan) to tetrahydro-2-methylfuran, a reaction that served as the starting point for the development of an accessible method for the synthesis of numerous γ-oxides.

Exceptional interest is presented by the fundamental investigations of Zelinsky and his students on the chemistry of proteins and of their component amino acids. His first investigation as a student was already directly related to this field.

In these investigations Zelinsky developed a new simplified method for the synthesis of α-amino acids by the action of an aqueous solution of ammonium chloride and potassium cyanide on aldehydes and ketones. By this cyanhydrin method a whole series of complex hydroxy-amino acids were obtained, and their role in the building of protein molecules constantly engaged Zelinsky's attention. His cyanhydrin method is now a classical one for the synthesis of α-amino acids, and it has passed in this form into textbooks and handbooks throughout the world.

The problem of the structure of proteins has been the subject of close attention for more than a century.

The remarkable investigations of N. D. Zelinsky and his talented teams of students and coworkers, among whom we may make particular mention of V. S. Sadikov, N. I. Gavrilov, N. A. Shlezinger, E. F. Dengin, I. V. Kulikov, A. L. Annenkov, A. B. Silaev, M. A. Prokofyev, and M. M. Botvinnik, have made an exceptionally valuable contribution to the study of protein structure. Zelinsky approached this field for the first time with the criteria and procedures afforded by new methods of synthesis and catalysis, and by his investigations he brought about a real revolution. By the application of his original method of high-pressure hydrolysis to the study of protein molecules, he showed that in most cases the primary hydrolysis products of proteins formed in presence of dilute acids and alkalis as catalysts were heterocyclic compounds, piperazinediones.

On the basis of his investigations over many years (they were begun in St Petersburg in 1912) on high-pressure hydrolysis, Zelinsky, in conjunction with V. S. Sadikov, worked out a theory of the cyclic structure of protein molecules. In subsequent investigations with N. I. Gavrilov and others, he unified his piperazinedione theory with E. Fischer's polypeptide theory, and so solved one of the most difficult problems concerning the fundamental microstructure of protein.

The research activities of N. D. Zelinsky form a brilliant example of innovation in science; he possessed in the highest degree that feeling for the new which is the powerful prime mover in progress. Foreseeing the great importance that radioactive radiations would have in scientific investigation and in practical applications of the highest importance to the state, Zelinsky, already in 1922, studied the effects of radium radiation on cyclohexene. The results of this work were communicated by Zelinsky to the third Mendeleev Congress on Pure and Applied Chemistry under the title "Decomposition of Hydrocarbons by the Energy of Radiation from Radium".

Zelinsky was a pioneer in the USSR in the study of various reactions at very high pressures (higher than 1000 — 2000 atm), and in 1939 he, together with L. F. Vereshchagin, established the Super-high Pressure Laboratory in the Institute of Organic Chemistry of the USSR Academy of Sciences. At the present time the reactions of a great variety of organic substances are being studied in this laboratory over a wide range of pressures (3000 — 50,000 atm).

In a short memorial sketch it is impossible to discuss, even schematically, the results of the extensive and important investigations of N. D Zelinsky. We should like to discuss his original work on the origin of petroleum, his remarkable investigations with Ya. T. Eidus on the catalytic synthesis of artificial liquid fuel from carbon monoxide and hydrogen, his promising researches on the catalytic condensation of acetylene to aromatic hydrocarbons, and the extremely interesting, though for some reason not very well-known, work on the synthesis of naphthenic acids and the study of their chemical nature. It would be desirable to describe Zelinsky's investigations over many years on the conditions for the synthesis of ketones of the cyclohexane and cyclopentane series (reactions formally analogous to the Friedel —Crafts reaction in the aromatic series), which were carried out by him in conjunction with E. S. Przhevalsky, S. S Nametkin. L F. Gutt, B. M. Berkengeim, and, particularly, E. M. Tarasova. One would have to describe Zelinsky's investigations on the catalytic synthesis of chloroprene, work on the catalytic desulfurization of petroleum and shale distillates, on the chemical nature of distillates from sapropelite tar, on the deparaffination of petroleum, on the gasolinization of petroleum, on the development of interesting syntheses of dimethylindigo, of phenol from chlorobenzene, acetone from acetylene, and phthalic anhydride by the catalytic oxidation of naphthalene.

It would be important to note also Zelinsky's investigations on the chemistry of hormones of the androsterone group (with M. I. Ushakov), the remarkable syntheses of branched carboxylic acids of the aliphatic —alicyclic series having an antitubercular bacteriostatic effect (with L. S. Bondar), and his new method for determining fats in an animal organism.

We must refer also to Zelinsky's investigations in biochemistry: his remarkable work on the elucidation of the causes of hydrogen sulfide fermentation in deep zones of the Black Sea, which is associated with the leading part that he played in the 1891 expedition on the gunboat "Zaporozhets"; his investigations on the chemical nature of the organizer responsible for the growth of secondary limbs on the axolotl; and other very interesting investigations in this attractive field.

The list of N. D. Zelinsky's important investigations could be continued further without any particular difficulty.

These extensive contributions to science, the whole of this great scientific feat, N. D. Zelinsky performed in close association and collaboration with his numerous students and collaborators, whom he painstakingly trained in the best traditions of foremost Russian science.

In the course of his purposeful scientific research work N. D. Zelinsky created the greatest school of organic chemistry in our country.

Up to the very last days of his life N. D. Zelinsky was closely associated with his students: Academicians A. N. Nesmeyanov, B. A. Kazansky, A. A. Balandin, Corr. -member K. A. Kocheshkov, Doctors of Chemical Sciences Yu. A. Arbuzov, P. P. Borisov, B. M. Berkengeim, N. I. Gavrilov, G. D. Galpern, Ya. I. Denisenko, K. P. Lavrovsky, R. Ya. Levina, Yu. G. Mamedaliev, S. S. Novikov, G. S. Pavlov, A. F. Plate, S. R. Sergienko, M. B. Turova-Polyak, N. I. Shuikin, Ya. T. Eidus, Yu. K. Yuryev, Doctor of Physicomathematical Sciences L. F. Vereshchagin, Candidates of Chemical Sciences L. S. Bondar, M. M. Botvinnik, G. R. Gasan-Zade, N. V. Elagina, P. G. Ivanov, E. I. Margolis, G. M. Marukyan, D. A. Morozova, I. A. Musaev, N. A. Poddubnaya, M. A. Prokofyev, S. E. Rank, A. B. Silaev, E. M. Tarasova, A. N. Titova, I. I. Tits-Skvortsova, S. I. Khromov, E. F. Tsintsevich, E. M. Shankhazarova, M. V. Yushke-vich-Gaverdovskaya, M. S. Eventova, and many others. The list of students and coworkers with which N. D. Zelinsky has published scientific papers contains more than 150 people.

Apart from his students and coworkers, Zelinsky always had many friends and admirers among eminent men of science and art.

Zelinsky was always a convinced supporter of well-harmonized team work in scientific work. Already in 1922 in his concluding address at the close of the third Mendeleev Congress he said: " The most important and fundament-al problems with respect to our concepts of nature require joint investigations for their solution: mathematicians, engineers, physicists, chemists, biologists, bacteriologists, medical men, mineralogists, geologists, and even astrono-mers must take part, for the microcosm of chemical molecules and the structure of atoms are bound to reflect in themselves elements of the structure of the universe".

In the Soviet Union it would be difficult to find a higher chemical teaching establishment, a research insti-tute, or a large chemical plant in which no student of Academician Zelinsky or of his students or coworkers was to be found.

As a true patriot of his great Fatherland, N. D. Zelinsky always carried out much responsible social work. It may be said without exaggeration that in the ranks of the older generation of scientists Zelinsky was one of the most eminent social workers, carrying on the best traditions of our progressive Russian intelligentsia.

Already under the reactionary political conditions of the Tsarist regime, N. D. Zelinsky was a progressive uni-versity worker. As an advocate of higher education for women, he organized at the end of the nineties an organic chemistry department in connection with the higher courses for women that were then starting in Moscow, and he was the first director of the department. He took an active part in the organization of the Shanyavsky People's University in Moscow.

From 1893 onward, N. D. Zelinsky took an active part in the work of the Moscow Society of Investigators of Nature, the oldest such society in the country, and from 1935 to the end of his life he was president of this society. In 1921 he was elected an honorary member of this society.

From the nineties of the last century onward Zelinsky joined in the activities of the Society of Amateurs in Natural Science, Anthropology, and Ethnography, the Kh. S. Ledentsov Society for the Encouragement of Progress in Experimental Science and its Practical Application, and particularly the Russian Physicochemical Society. From 1934 until his death he took a leading part in the D. I. Mendeleev All-Union Chemical Society, which is the successor to the Russian Physicochemical Society. Here also Zelinsky rightly earned the title of honorary member of the Society.

Even in his declining years, N. D. Zelinsky did not discontinue his scientific, teaching and social work. A fervent patriot of our great Fatherland, he responded quickly and directly to all the social and political events of our time, actively participating in the struggle of progressive humanity for peace. As early as August, 1950, he wrote in the journal "Technology for Young People": "I wish to add my voice to those of hundreds of millions of honorable people on our planet who understand that it is not sufficient simply to wish for peace, and that it is necessary actively and passionately to struggle for peace and tranquillity on the earth". He wrote further: "We scientists cannot remain to one side and watch in indifference how the barbarians of the twentieth century are preparing to set a new worldwide conflagration going and to strew the cities of the world with atom and other bombs in order to achieve their mad and fantastic purpose of world domination".

N. D. Zelinsky was an exemplary man and citizen, who provided an example of the very highest, truly socialist productivity of labor, worthy of imitation in every way. Throughout the whole of his long life he con-fidently moved on toward the summits of his favorite science, and to the end he devoted his science to the service of his great people and to the general task of constructing a communist society.

Together with the chemical society of our flourishing Fatherland we bow with feelings of the deepest respect in memory of the eminent Soviet chemist Academician Nikolai Dmitrievich Zelinsky.

A. N. Nesmeyanov
A. V. Topchiev
B. A. Kazansky
N. I. Shuikin

A. M. BUTLEROV

(In celebration of the 125th anniversary of his birth)

September 6, 1953, saw the completion of 125 years since the birth of the great Russian chemist, Aleksandr Mikhailovich Butlerov, one of the founders of modern organic chemistry and author of the theory of the chemical structure of organic compounds, which for more than ninety years has served, and still continues to serve, as the basis of all theoretical and experimental investigations in organic chemistry.

A. M. Butlerov was born on August 25 (September 6, New Style), 1828, in Chistopol in the province of Kazan, and he spent his childhood on his father's estate. In 1844 he left the First Kazan Gymnasium and began to attend lectures at the Department of Physics and Mathematics of the Faculty of Philosophy at Kazan University. He was not accepted as a student of the university until the next year, when he attained the age of seventeen. At the university Butlerov took a great interest in the natural sciences biology and chemistry. His interest in biology was reflected in his choice of subject for his candidate's thesis: "Butterflies of the Volga – Ural Fauna". His interest in chemistry developed in his student years while working in the chemical laboratory under Professors N. N. Zunin and K. K. Klaus. On completing his course at the university, Butlerov, at the request of the university council, gave courses in chemistry, physics, and physical geography to students of various faculties.

In 1851 Butlerov defended his Master's thesis on the theme "The Oxidation of Organic Compounds", and in 1854 he defended his Doctor's thesis, which was entitled "Ester Oils". On September 25 he was elected by the council as extraordinary professor of chemistry, and from that time until 1859, when he went to St. Petersburg, his scientific and teaching activities were associated with Kazan University.

Butlerov's theses are of the nature of reviews or compilations, and he did not publish them. His first experimental investigations, which were not unified by any common concept, were published during 1852 – 1857, and his first public discussion of a theoretical question occurred at Paris in 1858, when he read a paper, which has not been published, to the Paris Chemical Society on the constitution of substances. Some of the material contained in this paper was incorporated in Butlerov's article entitled "Observations on A. S. Couper's New Chemical Theory". In this article he develops ideas concerning carbon ("mechanical") types or "types of molecular structure", and he points out that "the time has come for us to go further than Gerhardt".

While abroad in 1857 – 1858, Butlerov began a series of investigations on methylene derivatives, which were continued further over a number of years at Kazan and St. Petersburg. He prepared methyleneiodide (and later, the bromide and chloride), and from this the diacetic ester of methylene glycol, which, however, did not give methylene glycol itself when hydrolyzed. An attempt to prepare the oxalic ester led to the isolation of a polymer of formaldehyde, which Butlerov called "dioxymethylene". By the action of ammonia on this substance, hexamethylenetetramine was prepared for the first time, and by the action of lime water a sugarlike substance "methylenitan". In this way the first laboratory synthesis of a carbohydrate was performed. The attempts made in the course of these investigations to isolate methylene in the free state were not successful: ethylene and its homologs were always formed.

In 1858 A. M. Butlerov was elected as an ordinary professor of Kazan University, and at the beginning of 1860 he was appointed rector. He occupied this post for three years, and it was with great difficulty that he managed to free himself from his heavy administrative duties.

In 1861 Butlerov set off on his second foreign mission, and at the Thirty-sixth Congress of German Physicians and Naturalists he read a paper on "The Chemical Structure of Substances", in which he stated the basic principles of the theory of structure.

In the fifties and early sixties of the last century, chemistry found itself, as Butlerov expressed it, "in an awkward situation", because the chemical theory then in existence could not satisfactorily interpret and unify the huge quantity of facts that had accumulated. Gerhardt's theory of types no longer satisfied chemists, because it was unable to explain a large number of addition reactions that had become known at that time and it permitted

large number of rational formulas for a given substance indicating the directions in which the substance must decompose when entering into various metathetic reactions. Also, most chemists acknowledged the concept of "constitution" of chemical compounds, which they understood, following Gerhardt, as the "true arrangement of the atoms in the molecule". For the determination, however, of this "true", i.e. spatial, arrangement of the atoms, the necessary means of investigation did not exist in the chemistry of that time, and for this reason many regarded such a problem as insoluble in principle. This had become the source of doubts in the possibility of forming sound theoretical views in chemistry, and of a tendency to agnosticism and return to empirical formulas. Kekulé wrote in the first volume of his textbook: "In chemistry we cannot even speak of true theory: all so-called theoretical considerations are based on probability and expediency." In 1861 he announced that he would give up the use of type formulas and use only empirical formulas in organic chemistry.

In his paper, A. M. Butlerov first criticized the type concepts and then spoke in favor of the hypothesis that atomicity (valency), a definite and unchangeable property of elements, could serve as a basis for the creation of a general theory of chemistry. In order to avoid superfluous hypothetical concepts, he proposed to set aside the hypothetical (at that time) "physical" atoms ("ultimate indivisible particles of elements") and operate with chemical atoms, by which he understood the smallest amount of an element that could enter into the composition of the molecule of a complex substance. Contrasting the mechanical arranging of atoms in a molecule with the concept of chemical structure, A. M. Butlerov defined the latter as follows in his paper: "On the basis of the concept that every chemical atom entering into the composition of a body takes part in the formation of the latter, acting there with a definite amount of the chemical force affinity that belongs to it, I define chemical structure as the distribution of the action of this force, as a result of which chemical atoms that directly or indirectly influence one another are united in a chemical particle."

The well known rule that the nature of a complex particle is determined by the nature, amount and distribution of the elementary components, may be changed. I consider, as follows: The chemical nature of a complex particle is determined by the nature of the elementary component parts, their amount, and the chemical structure." Later, speaking about chemical structure, Butlerov expressed himself more briefly and definitely, defining it as "the distribution of chemical bonds existing between atoms in a particle".

In the fundamental theses of the Butlerov paper, therefore, the concepts of atomicity (valency) of the elements, of the bonds between atoms in a complex molecule, and of the dependence of the properties of a complex substance on its chemical structure were brought together and unified. This made it possible to place chemical theory on sound ground and to link it directly with chemical experiment. If, in fact, the properties of a complex substance are determined by its structure, then we may form an opinion of its structure from its chemical reactions, and knowing the structure of a substance, we may predict its properties. In his paper A. M. Butlerov points out that reactions of all kinds (addition, decomposition, and metathesis) can be used for the determination of chemical structure, and he advances a number of empirical rules that may be used for this purpose. Without considering what concrete form must be taken for the outward expression of structural formulas, Butlerov advanced the view that only one structural formula was possible for each substance and that in the future, when the laws relating properties to structure became known, such a formula would express all the properties of the given substance. In his paper Butlerov raised, for the first time, the question of the mutual effects between atoms present in the same molecule, but not directly united, indicating that the views that he had advanced would help to provide an answer to this question in the future.

The work carried out by Butlerov in the years that followed had the object of developing the fundamental concepts of the theory of chemical structure and rendering them more precise. He considered, for example, questions concerning the differences in the nature of the valencies of carbon, nitrogen, and sulfur atoms, and he finally came to the conclusion that the hypothesis that the units of valency were different in nature was not correct. He studied also the reaction of phosgene with dimethylzinc, thus hoping to effect the direct synthesis of acetyl chloride or acetone, as the theory of chemical structure predicted; apart from substances containing the acetyl group, the main product of this reaction was found to be a crystalline compound that behaved like an alcohol, later shown to be tert-butyl alcohol.

An extremely important contribution to the development of the theory of chemical structure was Butlerov's fundamental work on "Various Explanations of Certain Cases of Isomerism". In this he shows, very clearly and convincingly, that the phenomenon of the isomerism of organic compounds is to be explained by difference in structure associated with identity in composition and molecular size, the differences in properties being, therefore, explained by differences in the mutual effects of atoms in the molecule; this is confirmed by numerous examples.

This paper must be associated with another large theoretical article "The Systematic Application of the Principle of Atomicity to the Prediction of Cases of Isomerism and Metamerism", in which he shows that from the point

of view of the theory of structure the prediction of the existence of isomers is only a matter of the construction of diagrams; he predicts the isomerism of saturated hydrocarbons and the existence, in particular, of isobutane.

It was at this period (1864) that Butlerov was working on a textbook of organic chemistry based on the theory of structure. In 1864−1866 the first edition of 'Introduction to the Complete Study of Organic Chemistry" appeared in Kazan, and this gave a new systematic treatment of organic compounds, extensively discussed the whole of the factual material available in the light of the theory of chemical structure, and developed its fundamental concepts, particularly that of the mutual effects of atoms in the molecule. In 1867−1868 the "Introduction" was issued in a German translation, and this edition helped greatly to spread the concepts of the theory of chemical structure beyond the frontiers of Russia.

At the same time, Butlerov's experimental work continued. A series of investigations was devoted to tert-butyl alcohol and tertiary alchols in general. Tert-butyl alcohol was prepared by Butlerov by the action of dimethylzinc on acetyl chloride; its properties were finally established, and various derivatives were synthesized, for example, the acetic ester and tert-butyl iodide; isobutane and isobutene were prepared, the synthesis of the former being particularly important, since it confirmed Butlerov's prediction of the existence of isomerism among saturated hydrocarbons, and the actual nature of this isomerism was explained from the point of view of the theory of structure; with isobutene (2-methylpropene) the reaction of polymerization was observed for the first time. To this same period (1867) belongs work on the synthesis of alcohols from 2-iodoethanol and dialkylzincs; the unexpected formation of secondary alcohols instead of the primary alcohols predicted by the theory of structure, led Butlerov to the conclusion that during this reaction there occurs an intramolecular rearrangement, which is also explicable from the point of view of the theory of structure,

A large number of new experimental facts, established not only by Butlerov, but also by other chemists in Russia and abroad, strengthened the foundation of the theory of chemical structure and helped it to become more and more widely known. With increasing frequency, however, cases occurred in which the name of A. M. Butlerov was ignored in publications concerned with matters relating in one way or another to the theory of structure. While remarking on the large number of examples that had appeared which confirmed the correctness of his theoretical views, Butlerov pointed out that "all this, however, does not prevent many foreign chemists from making insufficient acknowledgement of the part that I played in the development of the views that are now coming to be accepted in chemistry, and from frequently announcing as a new idea that which I have already announced". This position prompted him to go on a third mission abroad in 1868 in the hope of defending his priority by personal exchange of views with foreign chemists. This object, however, was not attained, and in foreign chemical literature the theory of structure is more often associated with the names of Kekule and Couper, than with that of A. M. Butlerov.

While he was abroad, Butlerov was elected to the chair of chemistry at St. Petersburg, and he began to lecture there on organic chemistry in January, 1869. In March, 1870, he was elected as an Adjunct of the Academy of Science, in December, 1871, he was elected as an Extraordinary Academician, and in January, 1874, as Ordinary Academician in Chemistry. The St. Petersburg period of his life was mainly devoted to activities in these two institutions, the Academy of Sciences and St. Petersburg University.

Butlerov's scientific work in the St. Petersburg period developed in the following directions. First of all he made a closer examination of the methylene derivatives that he had already investigated and showed that in the vapor state 'dioxymethylene" was the monomer "oxymethylene" (formaldehyde, CH_2O), whereas in the solid state it was the trimer "trioxymethylene", of cyclic structure; he showed also, that with ammonia gaseous formaldehyde forms the same hexamethylenetetramine as polyoxymethylene does.

A series of investigations followed that formed a continuation of those already begun at Kazan; they concerned tert-butyl alcohol, 1,1-dimethylpropionic acid, and other compounds that could be prepared from tert-butyl alcohol. It was shown that this alcohol could be readily prepared from isobutene by direct hydration in presence of sulfuric acid; it was also possible to prepare ethyl alcohol from ethylene, though under more severe conditions. Having obtained tert-butyl alcohol in large amounts and in a pure condition, Butlerov studied its oxidation with chromic acid mixture (acetic acid, acetone, and isobutyric acid are formed) and prepared, via the iodide and nitrile, a new isomer of valeric acid, 1,1-dimethylpropionic acid. From the acid chloride of this and dimethylzinc he synthesized pinacolone; he established the structure of this substance and so made a correct interpretation of the mechanism of the pinacolone rearrangement possible.

Continuing his investigations of isobutene and its reactions, Butlerov considered the question of the structure of unsaturated compounds and advanced the view that they contained multiple bonds, in support of which he provided convincing experimental evidence. He continued experiments on the polymerization of isobutene and other olefins in presence of sulfuric acid and boron trifluoride, and discussed the mechanism of the polymerization and the struc-

t.. of the polymers   The results obtained by Butlerov in this field were much in advance of the contemporary organic chemistry, and only very much later were they placed at the basis of technical processes for the synthesis of high-quality components of motor fuels. In one of the investigations, devoted to "biisobutylene", the concept of the tautomerism of organic compounds is developed; its treatment as reversible equilibrium isomerization is fully in accord with modern views on this phenomenon.

Butlerov's experimental investigations in the last period of his life stand somewhat apart from the previous ones. They concern some experiments with quinine and cinchonine, which helped in the elucidation of the structures of these alkaloids, and also a description of asarone, obtained from the plant Asarum europeum, and a study of its structure. A quite special position is occupied by his "Note on Atomic Weights" (1882), in which Butlerov discusses the question of the possibility of the atomic weight of an element varying according to the external conditions. He suggested that Prout's hypothesis, according to which the atomic weights of the elements are expressed by whole numbers with respect to hydrogen, may be true under conditions that have still to be defined, and that the usually observed departures of atomic weights from whole numbers result from nonobservance of these conditions. Experiments were begun with the object of finding these conditions and hence of experimentally confirming the complex character of atoms, but Butlerov did not succeed in completing them.

The two last theoretical papers of A. M. Butlerov are concerned with the theory of chemical structure. Toward the beginning of the eighties of the last century this theory occupied a leading position in organic chemistry, in which an enormous number of facts had accumulated which confirmed it and helped to develop it. Voices were still sometimes raised however — and they belonged to some of the most eminent chemists (Kolbe, Bertelot, Menshutkin) — expressing doubt in its correctness and fruitfulness. In his paper "Present Significance of the Theory of Chemical Structure" (1879), Butlerov showed in an exceptionally convincing manner that the theory was soundly based on an enormous amount of experimental material and had an extraordinary ability to predict. He countered objections made to the static character of structural formulas, pointing out that "we now regard chemical structure not as something dead and immobile; we consider, on the contrary, that it is endowed with constant movement, which is contained in its smallest particles, the individual relationships between which are undergoing continual changes, which integrate to a certain constant average result". He objected also to the idea that the theory of chemical structure was associated with the idea of the constant valency of elements, and he remarked that the theory was undeservedly condemned as denying the existence of mutual effect of atoms present in the same molecule, but not directly united.

In the second paper 'Chemical Structure and the Theory of Substitution' ", Butlerov attacked the idealistic basis of the theory of substitution and, comparing it with the theory of structure, concluded that its predictions were correct only when the chemical structures of the compounds under examination were already established. After these papers objections to the theory of structure ceased entirely, and it received general acknowledgement; it has maintained its leading role right up to the present day.

Throughout his whole life A. M. Butlerov combined his scientific activities with public and social activities. He was one of the leading members of the Russian Physicochemical Society from the time of its foundation, he took an active part in the congresses of Russian naturalists and physicians, gave public lectures to wide audiences, was one of the organizers of the higher courses for women, and was an active member of the Free Economic Society, in which he worked very vigorously on the development of rational apiculture in Russia.

In discussing Butlerov's public activities we cannot omit a reference to his articles directed against the then-dominant 'German party' in the Academy of Sciences — a party of academicians of non-Russian origin, who were trying to exclude the great Russian scientists from membership of the Academy. As an example of their reactionary activities we may refer to the nonelection of D. I. Mendeleev at the Academy elections of 1882, which prompted an exceptionally vehement protest from Butlerov in the article "Russian, or merely Imperial Academy of Sciences?", which was published in the newspaper "Russia".

On August 5 (17, New Style), 1886, A. M. Butlerov died suddenly, at the height of his creative activities. His role in the development of Russian and world chemical science cannot be overestimated. His name stands with those of Lomonosov and Mendeleev, and is an object of pride for our people.

THERMODYNAMIC STABILITY OF VARIOUS STRUCTURES

IN BINARY INORGANIC CRYSTALS

Yu. M. Golutvin

The question of the relative stabilities of various structures for simple binary inorganic compounds in the solid state is a very complex one. A study of this question shows that the problem of the thermodynamic stabilities of the crystalline phases referred to above may be solved by the use of the quantity ρ, the ratio of the univalent and crystal radii of an ion, which has been introduced into thermodynamic investigations by the author and Kapustinsky [1]. Their treatment permitted a quantitative relation to be found between heats of formation per gram equivalent $\dfrac{\Delta H^\circ}{W}$) and the values of ρ for the cation and anion. It was found that, for a series of compounds having a common cation or anion, $\sqrt{\dfrac{-\Delta H^\circ}{W}}$ increased, when comparisons were made along the groups and periods of Mendeleev's system.

When a compound is found, within the series under comparison, for which $(\rho_{cat} - \rho_{an}) = 0$, it has a maximum heat of formation per gram-equivalent ("inversion point"): on each side of this point $\sqrt{\dfrac{-\Delta H^\circ}{W}}$ for the other compounds fall on straight lines sloping downward. The general form of the graph for a series of compounds having a common anion and showing a point of inversion is given in Fig. 1 [the case of a comparison in a period in which the maximum range of variation of ($\rho_{cat} - \rho_{an}$) occurs]. The value of ρ expresses the effect of Coulomb forces on the dimensions of an ion of constant electronic configuration [2] and characterizes the relationship between the attractive and repulsive forces that the given ion exhibits with respect to the other ions in the crystal lattice.

The greater the value of ρ for a given ion, the greater, evidently, will be its ability to attract oppositely charged ions, and the less will be its ability to repel the electron atmospheres of these ions. In this connection, the ρ-values may be regarded as the polarizabilities of the ions.

The fact that, in a series of compounds under comparison, the compound for which $\rho_{cat} = \rho_{an}$ has the maximum heat of formation per bond shows that in this particular case the strongest bonds are formed, these, apparently, being of a predominantly ionic character. For compounds in which ρ_{cat} and ρ_{an} are not equal, the heat of formation per bond is less, indicating the increased "diffuseness" and lower ionic character of the bonds.

It follows from this that the difference $(\rho_{cat} - \rho_{an})$ may be regarded as a measure of the one sided polarization of ions in the crystal lattice. Hence, if the cation and anion have nearly equal ρ values, such compounds must have bonds that are essentially of the ionic type, because polarization phenomena cannot occur here to an appreciable extent. On the other hand, if ρ_{cat} and ρ_{an} are appreciably different in value, then, owing to the preferential polarization of one of the ions, the bonds must depart from the ionic type. If $\rho_{an} > \rho_{cat}$ [i.e $\rho_{cat} - \rho_{an}) < 0$], the cation will be polarized by the anion (see, for example, the distribution of electron density in Mg_2Si crystals, studied by Ageev and Guseva [3]. Owing to the lower deformability of cations, as compared with anions, the bonds must nevertheless preserve a still appreciable measure of ionic character.

When there is a considerable predominance of ρ_{an} over ρ_{cat}, we may expect the formation of structures of the Cac_2 type, in which polarization is reduced owing to the formation of voluminous multiple anions having a lower polarizability than simple anions. If $\rho_{cat} > \rho_{an}$ (i.e. $(\rho_{cat} - \rho_{an}) < 0$), the anions will be polarized by the cations to an extent that may be considerable, owing to the greater deformability of the anions, and this should lead to the formation of covalent structures; this includes also the case of compounds containing multiple cations (ρ_{cat} very much greater than ρ_{an}). These conclusions are confirmed by the experimental facts. Comparison of the data in the literature on the structures of the main classes of binary inorganic compounds and the types of chemical bonds that they contain [4,5,6,7,8] with the values of $(\rho_{cat} - \rho_{an})$ leads to the results given in Tables 1 and 2. Data for the calculation of ρ for certain other ions may be found in a paper by Kordes [9].

Table 2 does not include compounds of elements giving ions having 18-electron outer shells. Compounds of elements of this type will be examined separately.

Mapping of the electron density between the atoms provides the most reliable criterion for the determination of the type of chemical bond in the crystals. At present, however, very few such data are available for inorganic systems, and in the majority of cases it is necessary to deduce what type of bond is present in a particular crystal from indirect data (electrical conductivity, tendency to undergo electrolytic dissociation in polar solvents and in the melt, the type of crystal lattice, the interatomic distances, the angles between the bonds, melting and boiling points, tendency to undergo hydrolysis, mechanical properties, color, etc.). Owing to these circumstances and the presence of bonds of intermediate character, the assessment of types of bonds in various compounds, as given in Table 2, must be regarded as approximate and as expressing only the basic tendency that is characteristic of the particular compound.

The first row of Table 2 contains compounds having chemical bonds that we have described as covalent-ionic. These include structures having weak cation-anion bonds of appreciable ionic character and containing multiple anions having considerably stronger covalent anion-anion bonds. Such structures are most stable for compounds characterized by large negative values of $(\rho_{cat} - \rho_{an})$.

TABLE 1

Values of ρ for Various Ions

Ion	ρ	Ion	ρ	Ion	ρ	Ion	ρ	Ion	ρ	Ion	ρ	Ion	ρ
						Cations							
Li^{+1}	1.190	Be^{+2}	1.42	B^{+3}	1.75	C^{+4}	1.93	N^{+5}	2.27	O^{+6}	2.44	F^{+7}	2.72
Na^{+1}	1.154	Mg^{+2}	1.26	Al^{+3}	1.44	Si^{+4}	1.59	P^{+5}	1.74	S^{+6}	1.83	Cl^{+7}	1.88
K^{+1}	1.143	Ca^{+2}	1.19	Sc^{+3}	1.31	Ti^{+4}	1.41	V^{+5}	1.49	Cr^{+6}	1.56	Mn^{+7}	1.63
Cu^{+1}	1.076	Zn^{+2}	1.19	Ga^{+3}	1.31	Ge^{+4}	1.43	As^{+5}	1.51	Se^{+6}	1.57	Br^{+7}	1.59
Rb^{+1}	1.137	Sr^{+2}	1.17	Y^{+3}	1.29	Zr^{+4}	1.36	Nb^{+5}	1.43	Mo^{+6}	1.50	I^{+7}	1.54
Ag^{+1}	1.070	Cd^{+2}	1.18	In^{+3}	1.28	Sn^{+4}	1.35	Sb^{+5}	1.43	Te^{+6}	1.47		
Cs^{+1}	1.128	Ba^{+2}	1.13	La^{+3}	1.21	Ce^{+4}	1.26	Bi^{+5}	1.32				
Au^{+1}	1.060	Hg^{+2}	1.14	Tl^{+3}	1.21	Pb^{+4}	1.26						
						Anions							
F^{-1}	1.190	O^{-2}	1.26	N^{-3}	1.44	C^{-4}	1.59						
Cl^{-1}	1.126	S^{-2}	1.19	P^{-3}	1.32	Si^{-4}	1.42						
Br^{-1}	1.111	Se^{-2}	1.17	As^{-3}	1.28	Ge^{-4}	1.36						
I^{-1}	1.090	Te^{-2}	1.13	Sb^{-3}	1.20	Sn^{-4}	1.26						

Since the values of ρ_{cat}, when compared along the periods and groups of Mendeleev's system, increase in the directions left to right and bottom to top (Table 1), the structures indicated are found for compounds formed by cations of the first groups having low ρ values with anions having high ρ values. The carbides of elements of the first and second groups are actually acetylides, and contain multiple ions, C_2^{2-}, in which there are covalent bonds between the carbon atoms. For the alkali metals, owing to the considerable predominance of $\rho_{N^{3-}}$ over $\rho_{M^{1+}}$, the azides MN_3, containing multiple nitrogen ions, are more stable than nitrides of the normal-valency formula M_3N.

To this group of compounds we may assign also peroxides of metals of the first and second groups and structures having molecular interaction such as the higher peroxides (M_2O_4), polysulfides (M_2S_2), and polyhalides (MX_3) of metals of the first group of the periodic system. The field of existence of structures of this type is characterized by negative values of $(\rho_{cat} - \rho_{an})$ (about -0.3, and more negative values).
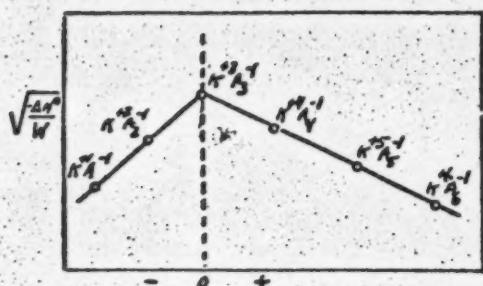
Fig. 1.

The field of $(\rho_{cat} - \rho_{an})$ values ranging from -0.3 to $+0.1$, is characterized by more stable structures of normal valency type in which there is a considerable ionic-bond contribution. The chemical bonds in these compounds are described in Table 2 as ionic. Here we find compounds having nearly equal values of ρ_{cat} and ρ_{an} (TiC, AlN, MgO, CaS, LiF, NaCl, etc.).

It is probable that certain carbides and nitrides having exceptionally high melting points and considerable chemical stability (SiC, TiN, and others) must be regarded as ionic compounds.

As has been shown in a series of investigations [10] the ions in highly symmetrical lattices of the NaCl or CsCl type may be regarded as undeformed, or as very slightly deformed to a mutually equal extent; the high symmetry of these lattices in itself prevents the development of polarization phenomena [11]. It follows that for compounds in which the values of ρ_{cat} and ρ_{an} are nearly equal and polarization phenomena are not greatly developed, the most "convenient" structures will be highly symmetrical structures of the NaCl or CsCl type. Actually, the majority of compounds described by us as "ionic" have cubic lattices [4,5]. When $(\rho_{cat} - \rho_{an})$ has positive values, greater than about 0.1 (in the case of compounds of elements of the last groups of the periodic table), the most stable structures are either metallic or covalent structures. In this field of $(\rho_{cat} - \rho_{an})$ values, metallic structures are found in compounds having anions with insignificant affinity for an electron (Mn_3C, Fe_3C, Cr_2N, $Cr N$, Mo_2N, MoN, etc.). These structures are characterized by stable metallic cation—cation bonds and weak, evidently essentially covalent, cation—anion bonds.

TABLE 2

Dependence of the Type of Chemical Bond in Binary Inorganic Compounds on the Value of $(\rho_{cat} - \rho_{an})$

| Type of bond	Range of variation of $(\rho_{cat} - \rho_{an})$	Classes of compounds				
		Carbides	Nitrides	Oxides	Sulfides	Halides
Covalent— ionic	-0.3	Li_2C_2 (-0.40) Cs_2C_2 (-0.46) MgC_2 Mg_2C_3 (-0.33) BaC_2 (-0.46) YC_2 (-0.30) La_2C_3 (-0.38)	$NaN_3(Na_3N)$ (-0.26) $CsN_3(Cs_3N)$ (-0.31)	$(Li_2O_2$; Na_2O_2; K_2O_2; K_2O; Rb_2O_2; Rb_2O_4; Cs_2O_2; Cs_2O_4; $BaO_2)$	Li_2S_3; Cs_2S_3	$(LiX_3$; $CsX_3)$
Ionic	-0.3 $\downarrow$ $+0.1$	Be_2C (-0.17) Al_4C_3 (-0.15) SiC (-0.00); TiC (-0.18); ZrC (-0.23); VC (-0.10); NbC (-0.16); MoC (-0.09)	Li_3N (-0.25) Be_3N_2 (-0.02); Ba_3N_2 (-0.31); AlN (0.00); LaN (-0.23) TiN (-0.03) ZrN (-0.08) VN $(+0.050)$ NbN (-0.01)	Li_2O (-0.07) Cs_2O (-0.13) MgO (0.00) BaO (-0.13)	Li_2S (0.00); Cs_2S (-0.06); MgS $(+0.07)$; BaS (-0.06); La_2S_3 $(+0.020)$	LiF (0.00); LiI $(+0.10)$; CsF (-0.06); CsI $(+0.04)$ MgF_2 (-0.07); BaF_2 (-0.06); $CaCl_2$ $(+0.06)$ $BaCl_2$ (0.00)
Metallic or covalent	$+0.1$ $\uparrow$	Cr_3C_2 (-0.33); Mn_3C $(+0.04)$ Re_2C_3 $(?)$; Fe_3C $(?)$; Co_3C $(?)$; Ni_3C $(?)$	Cr_2N, $Cr N$ $(+0.12)$; Mo_2N, MoN $(+0.06)$; Mn_3N_2; MnN_2 $(+0.19)$; FeN; Fe_4N $(?)$; Co_3N $(?)$; BN $(+0.31)$; $(CN)_2$ $(+0.49)$ Si_3N_4 $(+0.15)$; P_3N_5 $(+0.30)$	B_2O_3 $(+0.49)$; Al_2O_3 $(+0.18)$; CO_2 $(+0.67)$; SiO_2 $(+0.33)$; ZrO_2 $(+0.10)$; P_2O_5 $(+0.48)$; V_2O_5 $(+0.23)$; Nb_2O_5 $(+0.17)$; SO_3 $(+0.57)$; CrO_3 $(+0.30)$; MoO_3 $(+0.24)$; Cl_2O_7 $(+0.62)$; Mn_2O_7 $(+0.37)$; OsO_4 $(?)$	BeS $(+0.23)$; B_2S_3 $(+0.36)$; Al_2S_3 $(+0.25)$; CS_2 $(+0.74)$; SiS_2 $(+0.40)$; ZrS_2 (-0.17); P_2S_5 $(+0.35)$; MoS_3 $(+0.31)$; Re_2S $(?)$	BeF_2 $(+0.23)$; BeI_2 $(+0.33)$; $MgCl_2$ $(+0.13)$; MgI_2 $(+0.17)$; BF_3 $(+0.56)$; BI_3 (-0.66) $AlCl_3$ (-0.31); AlI_3 $(+0.35)$; CF_4 $(+0.74)$, CI_4 $(+0.84)$; SiF_4 $(+0.40)$; SiI_4 $(+0.50)$; PF_5 $(+0.55)$; SF_6, S_2F_{10} $(+0.64)$; TeF_6 $(+0.28)$; MoF_6 $(+0.31)$; OsF_8 $(?)$
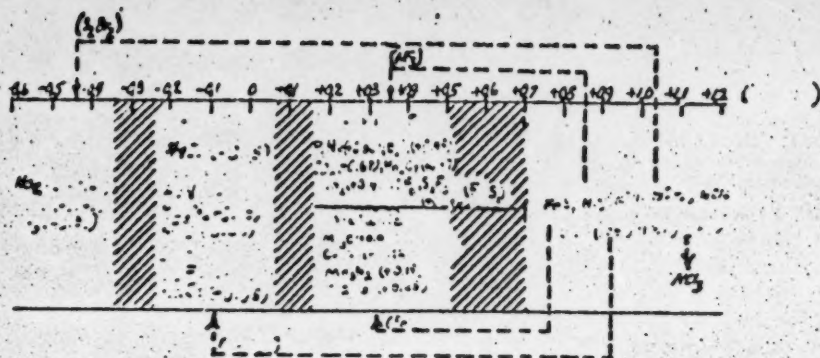
Fig. 2.

In the case of anions having an appreciable affinity for an electron, or of cations that are unable to form metallic bonds, the type of bond found is predominantly covalent (Mn_2O_7, MoF_6, F_3N_6, SF_6, etc.). Among the covalent compounds of this type, owing to the considerable predominance of ρ_{cat} over ρ_{an}, we meet also compounds having stable cation-cation bonds [$(CN)_2$, S_2F_{12}, etc.]. In accord with the powerful development of polarization phenomena occurring in compounds that we have described as "covalent", these have either coordination lattices of low symmetry, the geometry of which permits strong one-sided polarization, or molecular lattices [4, 5, 11]. For values of ($\rho_{cat} - \rho_{an}$) of greater than about -0.5-0.7, the stability of the structures under consideration falls to such an extent that the formation of compounds of the higher valency states of the cation becomes impossible, and this is very clearly manifested, owing to the low ρ-values of the halogens, in the halides of elements of the last groups of the periodic system (large ρ_{cat}) [$NF_5(+1.08)$; $NCl_5(+1.14)$; $MnCl_7(+0.50)$; $SBr_6(+0.72)$ etc.].

The stable compounds of these elements having not too large values of ($\rho_{cat} - \rho_{an}$), corresponding to various types of chemical bond, are formed here mainly at the expense of a reduction in the ρ-value of the cation attained by exhibition of a lower valency (the valency e of an ion is related to the value of ρ by the equation $\rho = e^{\rho(n-1)}$, in which n is the Born repulsion coefficient).

This dependence of the type of chemical bond in binary compounds of elements that do not give ions having 18-electron shells on the value of ($\rho_{cat} - \rho_{an}$) is illustrated by the scheme given in Fig. 2. The diffuse passage from one type of bond to another is represented by the wide shaded intermediate zones.

A special group of compounds is formed by elements that give ions having outer shells of 18 electrons. These elements show an enhanced tendency to form covalent bonds: in the whole range of ($\rho_{cat} - \rho_{an}$) it is difficult to find a compound that could be definitely regarded as formed mainly by any other type of bond. The list given below will illustrate this.

Cu_3P_2*	-0.51	$AuCl_3$*	-0.59.	ZnC_2	-0.40;	HgC_2*	-0.45
Cu_3N*	-0.36	Au_3N*	-0.44.	Zn_3N_2*	-0.25;	Hg_3N_2*	-0.30
$Ga N$*	-0.13	Ge_3N_4*	-0.01;	ZnO	-0.07;	HgO	-0.12
Ga_2O_3	-0.05.	GeO_2	-0.17;	SnO_2	-0.09;	As_2O_5	-0.25
Cu_2S	-0.11	Ag_2S	-0.19;	ZnS	0.00;	CdS	-0.01
GeS_2	-0.24	SnS_2	-0.16;	As_2S_5	+0.32;	Cu_2Cl_2	-0.05
Cu_2Br_2	-0.01;	$HgCl_2$	+0.01,	GaF_3	+0.12;	GaI_3	+0.22
$SnCl_4$	-0.22;	$AsCl_5$	+0.58; etc.				

In conclusion I express my deep gratitude to A. F. Kapustinsky for valuable help and advice.

SUMMARY

1.   A study has been made of the effect of the relationship between ρ_{cat} and ρ_{an} on the stability of binary inorganic compounds and the type of chemical bond that they contain.

2.   Highly stable compounds of normal-valency formula and having bonds of predominantly ionic character may exist   only for cations and anions having nearly equal ρ-values.

* Unstable, explosive compounds.

3.   In the case of compounds in which ρ_{an} is considerably greater than ρ_{cat} (high negative values of (ρ_{cat} – ρ_{an})), there occurs a lowering in the stability of compounds of normal-valency formula, and the covalent character of the bonds increases, leading in the limiting case to the formation of multiple anions.

4.   The characteristic structures of compounds for which ρ_{cat} is considerably greater than ρ_{an} (high positive values of (ρ_{cat} – ρ_{an})) are those having bonds of metallic or covalent type (sometimes structures containing covalent cation-cation bonds are found). The metallic type of bond is found when the anions have insignificant electron affinity, and the covalent type is found when the anions have considerable affinity for electrons or when the cations are unable to form metallic bonds with one another.

5.   Very high positive values of (ρ_{cat} – ρ_{an}) result in unstable structures; for such binary compounds stable structures can be found when the cation is in one of its lower valency states. Owing to the reduction in ρ_{cat} the difference (ρ_{cat} – ρ_{an}) is reduced to a value that ensures the stability of the compound.

6.   The approximate ranges of variation of (ρ_{cat} – ρ_{an}), corresponding to the predominance of the various definite types of chemical bond, have been given. The relationships considered refer to binary compounds of elements that do not form ions having 18-electron shells. The elements that give ions having 18-electron shells tend to form covalent bonds and apparently do not form compounds of predominantly ionic character.

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• See Consultants Bureau Translation, page 31.

ELECTRONIC PROCESSES IN CHEMISORPTION

COMMUNICATION 1*

F. F. Volkenshtein

In this paper a short exposition will be given of the results of a series of investigations by the author on the theory of heterogeneous catalysis, which have as their object the discovery of the elementary (micro-) mechanism of chemical process occurring at the surface of a crystal. In these investigations the problem of adsorption and catalysis is treated as a problem in physics and is regarded from the point of view of the modern theory of solids. In this paper the whole of the mathematical side of the matter is omitted. We consider here only the main results of our theoretical investigations, and then only from the qualitative side.

Every heterogeneous reaction includes, as obligatory intermediate stages, the stages of adsorption and desorption. The mechanism of a heterogeneous-catalysis process cannot be completely understood without an understanding of its intermediate stages. Hence, although the theory of adsorption can develop outside the theory of catalysis and independently of it, the theory of heterogeneous catalysis, on the contrary, can be built up only in organic association with the theory of adsorption. The construction of a theory of adsorption is the first step in the construction of a theory of catalysis. The present paper is devoted to certain questions in the theory of adsorption (adsorption as a stage of catalysis).

Various types of adsorption exist. The adsorption with which we are concerned in catalysis is generally the so-called "chemisorption", i.e. adsorption due to forces of a chemical nature, in which respect it differs from so-called "physical" adsorption, in which we are concerned with purely electrostatic forces (Van der Walls forces, electrostatic-polarization forces, electrical-image forces).

In their theoretical treatment, physical adsorption and chemisorption require essentially different approaches. In the case of physical adsorption the absorbed molecule and adsorbent can be regarded as two independent systems. The action of adsorbent on the adsorbed substance can be treated as a weak perturbation. In the case of chemisorption the adsorbed molecule and the lattice form a single quantum-mechanical system. The problem cannot now be solved by the methods of perturbation theory.

A solid that is an adsorbent in the process of chemisorption and acts as a catalyst is not an inert (nonparticipating) support on which the chemical processes develop, but is an active participant in these processes, taking part in the intermediate stages of the reaction as one of the components of the reaction. The whole system (reacting molecules plus the solid) must therefore be treated as a single whole.

In such a treatment the electrons of the crystal lattice are found to be direct participants in chemical processes occurring at the surface of the crystal. Moreover, in certain cases they are not only participants, but also regulators of these processes. In this paper we are mainly concerned with the part played by the electrons of the crystal lattice in chemisorption.

Chemisorption can interest us here not only as a stage of catalysis, and not only because it is an essential stage of catalysis, but also for its own sake, since chemisorption is the simplest case of a heterogeneous reaction. It is the reaction consisting in the combination of gas molecules with a solid, with which they form a peculiar unified system.

Chemisorption as a One-electron Bond

First of all let us examine the mechanism of the chemical combination of a gas molecule with a solid. In order to simplify the calculation (it can be made in the general case also), a suitable model must be chosen. We shall examine the simplest case [1, 2]. Let us take as our adsorbate an electropositive univalent atom, denoted by the symbol A. As adsorbent we shall take an ionic crystal formed from singly charged ions M^+ and R^- (M being a metal, and R a metalloid). These ions will be treated as point charges.

We shall introduce also two simplifying assumptions. First, we shall regard the surface of the crystal as an

ideal surface. In other words, we shall exclude the existence of defects of various kinds that are bound to exist in and on the surface of every real crystal, disturbing the strictly periodic structure of the lattice. Second, we shall ignore the existence of an electron gas, which is always present in some concentration or other within and on the surface of a crystal. Both of these assumptions will be removed (successively) in further treatment.

In our model we have a one-electron problem. The only electron is the valency electron of atom A. While atom A is sufficiently far from the surface of the crystal, our electron belongs to this atom (Fig. 1, a). When, however, the atom A is on the surface, its electron belongs not only to the atom A, but, strictly speaking, to the system as a whole.

Calculation shows that the valency electron of the atom A is then drawn out into the lattice to a greater or lesser degree. In other words, the electron cloud around the positive core of the atom A, which in the case of the isolated atom has spherical symmetry, is then deformed and to a certain extent drawn out into the lattice. This extension of the electron atmosphere into the lattice forms, in fact, the bond between the adsorbed atom A and the crystal. The bond is thus effected by the valency electron of the atom A. We obtain a bond of the same type as that in the molecular ion H_2^+; it is a one-electron bond (Fig. 1, b).

It can be shown that the strength of the bond between the atom A and the surface depends on how strongly the valency electron of the atom A is pulled into the lattice. The stronger the pull, the stronger the bond. This extension of the electron atmosphere leads, among other things, to the acquiring by the adsorbed atom A of a certain dipole moment, which is of purely quantum-mechanical origin; it is quite different in nature from the dipole moment that arises in physical adsorption and is due to the polarization of the adsorbed atom or molecule by the field of the lattice. We may point out that the value of the dipole moment arising in chemisorption can be shown to exceed, by a factor of several powers of ten, the value of that induced in physical adsorption.

Chemisorption as a Two-electron Bond

The degree of the extension of the electronic atmosphere from the atom A into the lattice is determined both by the nature of the atom A and by that of the lattice. In some cases this extension may be so small, i.e. the bond formed by atom A with the lattice may be so weak, that adsorption due to such a one-electron bond may not occur to an appreciable extent. In this case the free electrons of the crystal lattice itself may come to the rescue. Adsorption may occur by the introduction of a free electron of the lattice into the process.

Let us consider this case [3]. In the preceding calculation we neglected the presence of free electrons in the lattice. It is now necessary to take them into account. Let us return to our model, supplementing it by the introduction of a free electron on the crystal surface. We now have a two-electron problem: the first electron is the valency electron of the atom A, and the second is the free electron belonging to the lattice
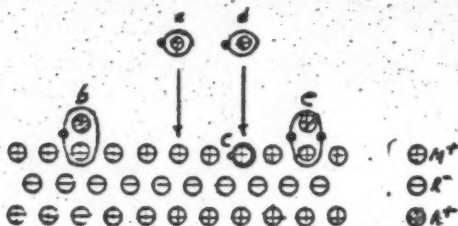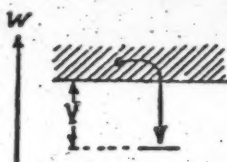

What does the presence of a free electron on the crystal surface signify? What does it mean when we say that in the surface conductivity zone there is an electron? It means that there is an electron on one of the surface M^+ ions, or, in other words, one of the M^+ ions of the surface layer of the lattice has been neutralized (converted into the neutral atom M) (Fig. 1, c).

Fig. 1.   Fig. 2.

When we say that a free electron moves in the surface conductivity zone, we mean that the electron moves from one M^+ ion of the surface layer of the lattice to a neighboring M^+ ion, and so moves over the surface of the crystal. In other words, we mean that the neutral state of the atom M wanders over the surface by transfer from one M^+ ion to the next.

It can be shown that the atom A, when placed on the crystal surface, creates a local level for the free electron of the lattice. This level is situated below the surface conductivity zone, as shown in Fig. 2. It plays the part of an "attachment" level for the free electron. If the lattice electron falls from the conductivity zone to the local level (as shown diagrammatically by the bold arrow in Fig. 2), this means that the electron has ceased to be free

and has become localized on the crystal surface near the place in which A is to be found. The atom A, therefore, plays the part of a "trap" for the free electron. It can be shown that there is then formed a fairly strong two-electron bond between the atom A and the lattice. Two electrons take part in this bond: the valency electron of the atom A and an electron of the lattice itself (borrowed from the family of free electrons).

The electron of the lattice and the atom A are then bound together by exchange forces. In this case these exchange forces are the adsorption forces holding the atom A on the surface and, at the same time, holding the electron of the lattice in the proximity of the atom A. We obtain a bond of the same type as that present in the H_2 molecule. The strength of the bond depends on how far the local level of A is below the surface. The lower the level (the higher the value of V in Fig. 2), the stronger the bond and the stronger the localization of the lattice electron.

As the atom A is removed from the surface of the crystal, the local level in Fig. 2 is drawn toward the zone (V is reduced), the exchange bond between the atom A and the lattice is weakened, and the lattice electron in the local level of A is gradually delocalized, i.e. its wave function becomes more and more smeared out. In the limit, when the atom A is infinitely removed from the surface, the local level is found to be drawn into the zone. The electron in this level is thus taken into the conductivity zone, i.e. completely delocalized and so returned to the family of free electrons.

All this can be graphically redescribed in terms of the model. Let us imagine that the atom A falls on the surface of the crystal, as shown in Fig. 1, a. If the free electron of the lattice then remains on one side without forming a link with the atom A, then, in general, adsorption does not occur. We are now ignoring the one-electron bond due to the valency electron of the atom A, as we are considering the case in which this bond is so weak that it may be neglected. If, however, the atom A, on coming to the surface, meets a free lattice electron, as indicated in Fig. 1, d the atom will take up the electron and become adsorbed. The atom A becomes attached to the surface, and the free lattice electron becomes attached to the atom; we obtain a two-electron bond (Fig. 1, e).

The free lattice electron acts, therefore, as an adsorption center. Let us state this in another way: a neutral atom M that is present among the M^+ ions of the surface layer serves as an adsorption center. Adsorption of the atom A on such a center results in the localization of this wandering center and consists in the formation of a quasimolecule AM having a characteristic two-electron bond.

The whole of this mechanism, which we have described in the language of the theory of solids, can be described in another, more chemical, language. An electron in the surface conductivity zone may be treated as a free (unsaturated) valency, wandering over the crystal surface. Actually, the metal ion M^+ in the lattice has a complete electron shell, whereas the neutral atom M contains, in addition to the complete shell, a single unpaired electron, i.e. an unsaturated valency. When these two valencies meet, mutual saturation occurs, and this leads to adsorption, i.e. to the chemical combination of the atom A with the crystal.

Activated Adsorption

Let us now examine the consequences ensuing from the concept of free electrons as adsorption centers [4, 5]. Such a treatment of adsorption centers leads us to ascribe a number of specific properties to them: 1) free adsorption centers are not localized on the crystal surface, but wander over the surface; 2) the number of adsorption centers does not remain constant, but increases as the temperature rises; 3) by the action of external factors on the lattice, it is possible (at a given temperature) to alter the number of adsorption centers artificially.

It should be noted that the concentration of electron gas at the surface of an ionic crystal is extremely low under normal conditions. From this it might appear that the surface would be able to accept only a negligible quantity of gas atoms. This, however, is not so: it may be readily shown that, as the surface becomes filled, more and more new adsorption centers arise as a result of transfer of electrons from the normal zone and the formation of a corresponding number of holes.

We shall denote the number of adsorbed atoms per unit area by $\underline{N}$; the concentration of free electrons in the surface conductivity zone, i.e. the number of free (unoccupied) adsorption centers, by $\underline{n}$; and the concentration of free holes in the normal surface zone by $\underline{n}'$. It will be obvious that n' is at the same time the total number of adsorption centers (free + occupied). It can be shown that under equilibrium conditions we shall have:

$$
\left.
\begin{array}{l}
n = {}^{1}/{}_{2}\left(\sqrt{N^2 + 4n_0^2} - N\right) \\
n' = {}^{1}/{}_{2}\left(\sqrt{N^2 + 4n_0^2} + N\right)
\end{array}
\right\} \tag{1}
$$

in which n_0 is the concentration of electron (or hole) gas in the case of a clean surface (i.e. when N = 0).

The relations expressed by Equations 1 are represented in Fig. 3. We see that the total number n' of adsorption centers increases as the surface coverage increases, i.e. as N increases, but the number $\underline{n}$ of free centers slowly falls. We always have a certain reserve of free adsorption centers on the surface which are able to accept gas atoms. It can be shown that, as a result, the differential heat of adsorption, which we shall denote by Q, also depends on the coverage, i.e. on N
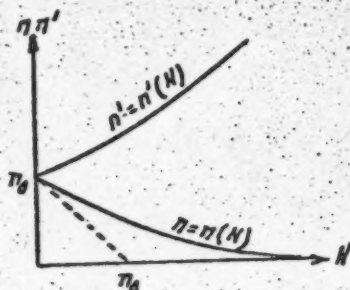

Fig. 3
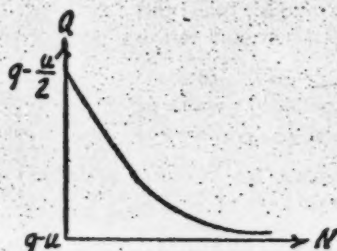
Fig 4

It may be shown that the relation between Q and N is expressed by the formula

$$ Q = q - \frac{u}{2} \left(1 + \frac{N}{\sqrt{N^2 + 4n_0^2}} \right) \tag{2} $$

in which q is the heat of adsorption for a separate atom, i.e. the energy of the bond between the adsorbed atom and the adsorption center, and $\underline{u}$ is the energy of formation of the pair (free electron + free hole), i.e. the work spent in the creation of each adsorption center.

The relation between Q and N, expressed in Equation 2, is represented in Fig. 4. We see that the differential heat of adsorption falls as the coverage increases, in spite of the fact that the surface is assumed to be homogeneous (adsorption centers of one kind only) and the interaction between adsorbed atoms has been ignored.

Let us now turn to the kinetics of adsorption. If adsorption proceeds sufficiently slowly and electron equilibrium in the lattice is established sufficiently rapidly so that electron equilibrium may be considered to exist throughout adsorption process, then for coverage as a function of time we obtain, as can be shown, the following equation, which is valid when the coverage is sufficiently low, i.e. at the beginning of the adsorption process:

$$ N = Ae^{-\frac{u}{2kT}} \cdot pT. \tag{3} $$

($\underline{p}$ is pressure, T absolute temperature, and A a constant, which can be analyzed further).

We thus arrive at Benham's law (with the index $\frac{1}{2}$), which often holds in practice and which is generally regarded as a criterion of heterogeneity of surface (in the given case the surface is homogeneous). We see (Equation 3) that heating does not retard the adsorption process, but, on the contrary, accelerates it. We obtain kinetics that are typical of so-called activated adsorption, the activation energy being

$$ \varepsilon = \frac{u}{2} . $$

To explain the way in which the exponential factor in the kinetic formula (Equation 3) arises — that, practically speaking, is the problem that the theory of activated adsorption sets out to solve. The origin of this factor is generally explained by introducing the concept of a potential barrier on the adsorption curve (Fig. 5). In our case there is no potential barrier. The actual number of adsorption centers, however, rises exponentially with temperature. Here lies the origin of the exponential factor in Equation 3.

In the usual theories of activated adsorption, which are concerned with a potential barrier at the crystal surf-
number of gas atoms striking the surface rises exponentially with the temperature, whereas the number of adsorption centers accepting these atoms remains constant. In our case, on the contrary, the number of accepting centers rises exponentially with the temperature, whereas the number of atoms striking the surface remains practically constant
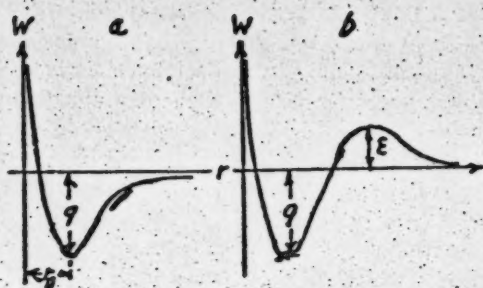
Fig. 5

At a given temperature the concentration of free electrons at the surface of the crystal, i.e. the concentration of adsorption centers, may be artificially changed as a result of external influences affecting the crystal. For example, irradiation of the crystal with photoelectrically-active light should lead to an increase in the adsorbing power of the crystal. Irradiation should also affect the kinetics, bringing about acceleration of adsorption. In fact, while we maintain the irradiation, we at the same time maintain an increased concentration of adsorption centers at the surface of the adsorbent.

Another factor affecting the concentrations of electron and hole gas in the crystal, is provided by impurities. The introduction of foreign donors increases, and the introduction of foreign acceptors diminishes, the concentration of electron gas. Impurities, therefore, should have an effect both on the kinetics of adsorption (accelerating or retarding adsorption) and on the adsorption equilibrium (increasing or diminishing the adsorbing power of the crystal).

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METALLIC COMPOUNDS *

I. I. Kornilov

At the basis of the science of alloys lies Mendeleev's periodic law and Mendeleev's ideas on the nature of alloys, both as solutions and as indefinite compounds [1] The study of alloys is also one of the main branches of physicochemical analysis, which was founded by Kurnakov [2] and is now being developed in the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences under the general direction of Academician Zazov [3] The chemical side of alloy science was referred to by Kurnakov as chemical metallography [4]. This field of science is now called alloy chemistry, or, as we propose to call it, metallochemistry [5].

The most important objects of metallochemistry are the study of the laws of formation of metal solutions and metallic compounds, and the application of these laws to the determination of the equilibrium diagrams of metal systems. The laws of formation of solid solutions of metals [5, 6, 7, 8], which are based on Mendeleev's periodic law, also relate in equal measure to the formation of metallic compounds. This paper is devoted to some questions relating to the formation of metallic compounds.

Classification of Metallic Compounds

The name "metallic compound" was first introduced by Kurnakov in 1899 when studying compounds formed between metals [9]. Kurnakov's term, metallic compound, is the one that most closely corresponds to chemical views on the nature of alloys. For these compounds, in place of the great variety of terms that are in use — intermetallic compound, "intermediate phase", and others — we consider it correct to preserve the name given by Kurnakov, "metallic compounds" [5].

The most general property of metallic compounds is that they are characterized by the metallic properties inherent in pure metals; they differ from ionic compounds in that the metallic bond is predominant: in metallic compounds atoms of different kinds are linked together in the crystal lattice predominantly by metallic bonds, which, unlike those in solid metal solutions, fix a constant stoichiometric ratio of atoms in the compounds. As a rule, metallic compounds have individual crystal lattices. Atoms of different kinds are arranged in orderly fashion in such a lattice. The strength of the chemical bond between atoms of different kinds in metallic systems that form compounds varies with the composition. This is reflected in the variation of the properties of alloys with concentration and in the nature of the composition — property diagrams. On these diagrams the compositions of compounds are shown as singular points.

Metallic compounds should be classified on the basis of the generally acknowledged classes of chemical compounds proposed by Kurnakov [2, 6]. A great variety of compounds was divided by him into berthollides, compounds distinguished by variable composition and absence of singular points on composition-property diagrams, and daltonides, compounds of constant composition and showing a singular point on composition-property diagrams.

Taking as our basis Kurnakov's principle of classification applied to metallic compounds, we may now single out the large group of compounds formed as a result of transformations of solid solutions. These compounds, which we call Kurnakov compounds (see below), may be of the berthollide or daltonide types. In considering questions concerning the formation of metallic compounds, it must be remembered that there is an undoubted connection between the formation of solid solutions and of metallic compounds. This connection can be readily traced by studying examples of the conversion of solid solutions into Kurnakov compounds and the gradual transition of compounds of the berthollide type into compounds of the daltonide type.

By studies of compounds of constant composition it is possible also to show how a given metal, reacting with elements of different groups of the periodic system, forms compounds of metallic or ionic character.

The enormous range of variation in the chemical nature of solid solutions and metal compounds, which is examined below, is subject to the fundamental principles of Mendeleev's periodic law, and is a consequence of this law. The concept of continuity in solid solutions is closely linked with the discreteness in the composition and properties of metallic compounds of constant composition, and the latter compounds are genetically associated with com-

pounds of the ionic type. This is a graphic proof of the dialectical character of chemical reactions between metals.
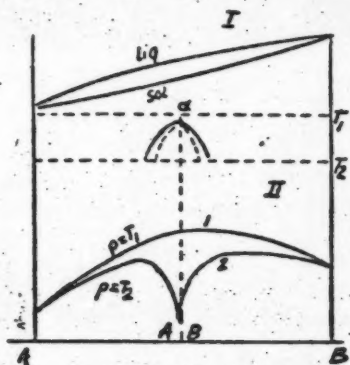
Kurnakov Compounds

It has been long established in metallochemistry that many solid metal solutions are stable only at high temperatures. In the course of slow cooling, these solid solutions yield metallic compounds. The classical demonstration of the occurrence of chemical processes in solid solutions was given by Kurnakov in his work on the copper - gold system. For the first time, in 1914, Kurnakov [10] established that when the solid solutions of this system were cooled slowly, two compounds, Cu₃Au and CuAu were formed. In the period of almost forty years that has passed since this discovery, similar compounds have been detected in numerous solid metal solutions. Whereas up to the time of Kurnakov's discovery the system copper - gold, in which these compounds were formed, could be regarded as exceptional, at the present time, on the contrary, a system consisting of solid solutions in which metallic compounds are not formed would be regarded as exceptional. Even in a system consisting of two metal analogs having almost identical atomic diameters, namely silver - gold, it has recently been established (1951) as a result of very long transformation times (about 1340 hours) in the range 300 - 450° that there are signs of the formation of two compounds, Ag₃Au and AgAu [11].

Although it is quite obvious that Kurnakov is the discoverer of metallic compounds in solid solutions, his priority is ignored in many foreign monographs on metallophysics. Foreign scientists call these compounds simply "ordered solid solutions", "arrangement of remote order", "superlattices". These same names have been translated literally into Russian to describe the concept. One is at a loss to understand how our scientists could pass over in silence the ignoring of Kurnakov's priority, when translating a number of monographs into Russian. In Pauling's book "Nature of the Chemical Bond" (translated by Ya. K. Syrkin) there are references to numerous investigations on these questions by foreign scientists, Tammann, Dehlinger, Bragg, Hume-Rothery, and others, but there are no references at all to the first and original investigations of Kurnakov in this field. In the book by Seitz, "Physics of Metals" (translated by E. L. Adrovich and M. P. Shaskolskaya), there are no references at all to Kurnakov's work in the discussions on solid solutions and ordered phases. In the interests of the establishment of the priority of Russian science in the discovery of compounds of these types formed from solid solutions, it will be just to name these compounds "kurnakov compounds". This general name can replace such indefinite terms as "ordered solid solutions", "superlattice", etc.

Among Kurnakov compounds there is a predominance of compounds of the daltonide type. They are distinguished by rapidity of formation, and characterized by ordered structure, characteristic type of crystal lattice, integral ratio of atoms, and a singular point on a composition-property diagram. Their singular points, corresponding to the compositions of Kurnakov compounds, are minima for resistivity and hardness (Fig. 1). The maximum rate of formation of such compounds from solid solutions corresponds exactly to the composition of the compound, and the rate therefore diminishes when one or other component is taken in excess [12].

Fig. 1 Melting point diagram (I) and composition-property diagram (II) for system of continuous solid solutions in which Kurnakov compounds are formed. Resistivity ρ : 1 — at temperature T₁ in the region of solid solutions; 2 — at temperature T₂ in the region of compound formation.

Definite regularities are to be observed in the stability of Kurnakov compounds based on any particular metal. These are determined by the position of the metal in Mendeleev's periodic system. If the temperature of formation of these compounds from solid solutions is taken as a measure of stability, it may be shown that it rises as the difference in the chemical properties of the reacting metals increases.

We may readily convince ourselves of the truth of this by considering, as an example, the formation of compounds from solid solutions of Group VIII metals, which have the greatest tendency to form compounds from continuous solid solutions.

Thus the following Kurnakov compounds are formed from continuous solid solutions of iron with metals of Group VIII: FeNi₃ FeCo. FePd₃ FePd and FePt. The formation temperature of these compounds increases regularly from

FeNi$_3$ (580°), through FePd (1120°), to FePt (1320°). This corresponds to the rise in atomic number of the Group VIII element.

If we compare the formation temperatures of Kurnakov compounds of iron with metals of the same row, but of various groups, for example, in the systems: iron - nickel, iron - cobalt, iron - chromium, and iron - vanadium, we can readily convince ourselves of the truth of this rule. In the last two systems also, compounds are formed from solid solutions (FeCr and FeV). The temperature of the formation of these compounds rises from 580° for FeNi$_3$ to 930° for FeCr, and to 1230° for FeV, i.e. rises regularly from compounds of Group VIII elements to those of elements of Groups VI and V.
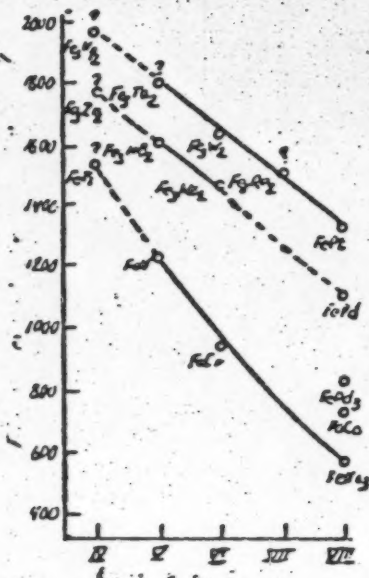
Fig 2 Variation of the formation and melting points of some compounds of iron with the positions of the elements in the rows of the periodic system.

The relation of the formation temperatures of Kurnakov compounds to the positions of elements in the periodic system, which we were the first to establish, is illustrated by the data given in Fig 2, in which the formation temperatures of all metallic compounds formed by iron with metals from Group IV to Group VIII are shown. At the moment we are considering the formation temperatures of only Kurnakov compounds.

As will be seen from Fig. 2, a regular rise in the temperatures of formation of Kurnakov compounds occurs in series of iron compounds: from the compound with nickel, through that with palladium, to that with platinum (metals of Group VIII); and from the compound with nickel, through that with chromium, to that with vanadium (metals of Groups VIII, VI, and V).

With increase in the difference in the electronic structures of the metals, corresponding to their increased separation in the periodic system, the temperature stability of the compounds rises, until they become stable right up to the melting point, in which case they are formed directly on crystallization of the melt.

A clear example of such behavior is found in the interaction of iron and titanium (Group IV element). Iron forms only limited solid solutions with this element, and metallic compounds, Fe$_3$Ti and FeTi of high melting point are formed directly on crystallization of the melts (see Fig 2). Hence, with increase in the chemical difference between metals, in accordance with their positions in different groups of Mendeleev's periodic system, the kind of interaction changes. Correspondingly, in metal systems the mutual solubility in the solid state diminishes, and the tendency to form metal compounds directly from melts increases. Hence, the limited solid solutions in metal systems correspond in most cases to the limits of the existence of metallic compounds in these systems, and serve as the boundaries for the transition from solid solutions to metallic compounds. Here in graphic form we see a manifestation of the dialectical law of the transition of quantitative changes into a new quality. The continually rising concentration of the dissolved element and the increase in the strength of the chemical bond at a definite atomic ratio leads to a sudden jump: to the formation, either from solid or from liquid solutions, of metallic compounds of constant composition, having new lattice parameters and new properties. Between solid metal solutions and compounds of constant composition there is, however, an intermediate class of metallic compounds called compounds of variable composition.

Metallic Compounds of Variable Composition (Berthollides)

In metal systems we find compounds that form an intermediate class, which corresponds to their different degree of stability. These compounds differ from solid solutions based on particular metals by having a different type of crystal lattice and a break in continuity of composition. They differ also from compounds of constant composition in that they do not conform to the law of constant and multiple proportions and do not correspond to definite stoichiometric relationships. On composition-property diagrams (Fig 3) these compounds have no singular points, and their compositions are characterized by a somewhat extensive range of homogeneity. Compounds of variable compositions are not subject to the laws applying to valent compounds.
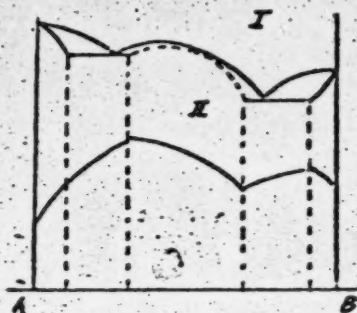
Substances of this type form an intermediate class of metallic compounds. They are intermediate between continuous solid solutions and metallic compounds of constant composition.

These metallic compounds of variable composition have all the properties of metals. They may therefore be called metallic compounds of variable composition (berthollides).

The formation of such compounds is again related in periodic fashion to the distribution of the elements by groups, and to the ratio of atomic diameters and of concentrations of valency electrons. The type of the crystal structure of such compounds is often determined by the ratio of the number of valency electrons to the total number of atoms in the elementary cell. These compounds have therefore been called "electronic compounds". The laws of their formation have been studied by Konobeevsky [13] and other investigators.

In many metallic compounds of variable composition, such as the β-phase in the copper-zinc, silver-zinc, and other systems, the features characteristic of variable composition are preserved only at high temperatures.

Fig. 3 Melting point diagram (I) and composition - property diagram (II) for a system in which a compound of variable composition (berthollide) is formed

At lower temperatures, these berthollide phases of variable composition yield Kurnakov compounds having ordered dispositions of atoms in their lattices and characteristic singular points on composition - property diagrams. An example of such a compound is the CuZn, or so-called β-phase, in the Cu-Zn system [14]. The most typical transformation of this sort is that of the β-phase in the silver-Zn system into a Kurnakov compound corresponding in composition to AgZn.

An interesting example of the transformation of compounds of variable composition into a Kurnakov compound is that of the γ phase of variable composition in the aluminum-magnesium system into the compound of constant composition Al₃Mg₄, as established by Mikheeva [15]. The author writes that at low temperatures the γ-phase is the carrier of the compound Al₃Mg₄, which only at high temperatures, close to the onset of melting, is in the state of complete dissociation.

In the course of the gradual transition from compounds of variable composition to compounds of constant composition, a new transitional class of metallic compounds makes its appearance. These compounds are characterized by the formation of peculiar crystal structures, in which the valency of atoms of a given element changes as the composition of the solid phase changes. Typical examples of such compounds are those having the so-called nickel arsenide structure (NiAs). This homologous group of phases, as Makarov calls it [16], is characterized by a variable number of atoms in the elementary cell, corresponding to a continuous change in the valencies of the atoms as the composition of the given phase changes. It should be noted that compounds of this sort do not lose their metallic properties and therefore can be called metallic compounds.

Metallic Compounds of Constant Composition (Daltonides)

The most typical metallic compounds of constant composition having whole-number ratios of atoms are formed between electropositive and electronegative elements. It was with these compounds that Kurnakov began his systematic investigations of compounds between metals, and it was to these that he first applied the name of "metallic compounds" [9]. These compounds are formed between, for example, an alkali or alkaline-earth metal and a more electronegative metal of Groups IV B, V B, or VI B.
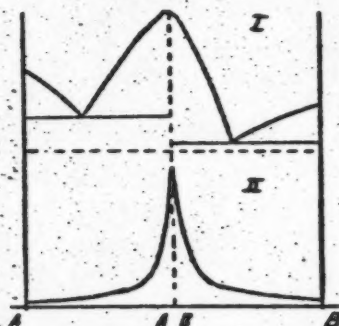
Fig. 4 Melting-point diagram (I) and composition-property diagram (II) for a system in which a compound of constant composition (daltonide) is formed

Compounds of this type are formed directly from liquid solutions. On melting-point diagrams they show maxima, and their compositions correspond to whole-number ratios of atoms. On composition-property diagrams these compounds show singular points (Fig. 4), corresponding to the constant compositions of the compounds. Compounds of this type were called "daltonides" by Kurnakov [2].

Unlike Kurnakov compounds, such metallic compounds, when they do not form solid solutions with the components, show a maximum resistivity and hardness (see Figs. 1 and 4). The resistivity of such compounds is sometimes 500-1000 times as great as the same property for the components (in the case of Mg₂Sn, for example). This indicates the reduction of the number

of free electrons and the formation of a bond by the valency electrons.

The relative stabilities of compounds of constant composition, like that of Kurnakov compounds, is determined by the chemical properties of the interacting metals and depends on their positions in the periodic system. If in this case we take the melting point of a compound (the temperature of its formation from liquid solution) as a measure of the relative stability of the bond it contains, then the existence of such a relationship can be shown by an examination of a large number of metal compounds. For example, by an examination of the compounds of magnesium we may show how their melting points vary according to the position of the second element in the Groups, and how the gradual quantitative change in the character of the chemical bond in metallic compounds results in a new quality: in a transition to compounds of the ionic type. The metallic compounds of magnesium were studied systematically by Stepanov [17].

In Fig. 5, on the left, melting-point curves of metallic compounds of magnesium with elements of Groups IB, IIB, and IIIB are shown. We may conclude from these curves that the formation temperature or stability of compounds of magnesium with elements of all three groups rises as the atomic number increases. The position is particularly clear for compounds with elements of Groups I and II, and as regards the Group III elements, although there are no experimental data on the formation temperatures of the compounds Mg_3In_2 and Mg_3Ga_2 (arbitrary values are given), it may be assumed that the order shown will be confirmed in the future.
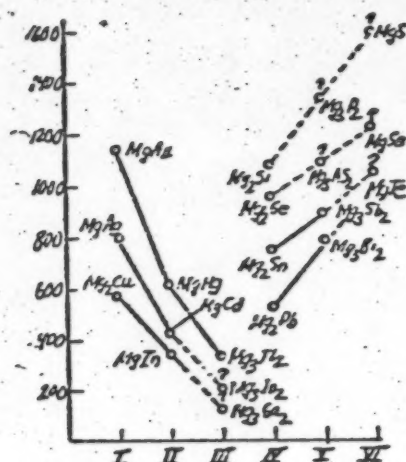
The curves on the right of Fig. 5 relate to compounds of magnesium with elements of Groups IV B, V B, and VI B. An analysis of data on compounds formed by magnesium with elements of these groups indicates that these compounds are subject to valency rules. As the number of the group increases, they gradually pass over into ionic compounds.

For the final establishment of the relation between the melting points of these compounds and the positions of the reacting elements in the periodic system, the necessary complete experimental data are unfortunately not available. Information is available on the melting points of all compounds of magnesium with elements of Group IV and of individual compounds of magnesium with elements of Groups V and VI. An examination of compounds formed with elements of Group IV, which are of the Mg_2R type, shows that the formation temperature of these compounds falls as the atomic number of the reacting element rises. The same order is found for the compounds of the type Mg_3R_2, formed with the Group V elements bismuth and antimony. The absence of data on the temperatures of formation of compounds of magnesium with arsenic, phosphorus, nitrogen, and sulfur and its analogs makes it impossible to reach a final conclusion regarding the role of the elements of Groups V and VI. Nevertheless, it may be assumed that the melting points of compounds of magnesium with these elements will fall as the atomic number of an element of a given group increases.

Fig. 5. Dependence of the melting points of some magnesium compounds on the positions of elements in the rows of the periodic system.

All compounds formed by magnesium with elements of Groups I-III have metallic properties: they are metallic compounds. Metallic properties are possessed also by compounds of magnesium with Group IV elements, and the same properties are characteristic of the majority of the compounds formed by magnesium with Group V elements.

Compounds of some Group VI elements, such as sulfides, selenides, and tellurides of magnesium, which are to a considerable extent ionic compounds, still preserve certain metallic properties. Compounds of this type belong to the class of so-called semiconductors. Compounds formed by magnesium with halogens (Group VII) are purely ionic compounds: the metallic character of the bond has completely disappeared, and they are classical examples of salts.

Thus, by an examination of compounds formed by magnesium with elements distributed over the various groups of the periodic system, we may convince ourselves of the gradual change of the metallic character of the bond in these compounds and their transition to ionic compounds: a transition from purely metallic magnesium compounds to

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magnesium salts.

The dependence of the relative stabilities of metallic compounds formed from melts on the positions of the reacting elements in the periodic system can be demonstrated also by examples based on compounds of other metals. We have examined above the dependence of the formation temperatures of Kurnakov compounds (the example taken being iron) on the positions of the elements in the various groups (Fig. 2). In Fig. 2 data are given also of the melting points of compounds formed by iron with metals of Groups IV-VIII. The three curves given in Fig. 2 for elements of the 4th, 6th, and 8th rows, uniting points representing the melting points of compounds of iron with Group IV-VIII metals, prove convincingly, in spite of the absence of some experimental data, that this relationship holds. The melting points of metallic compounds of iron rise regularly from Group VIII to Group IV and, in each group, from low to high atomic number. The relative similarity or difference between the two components determines whether the formation of the iron compound occurs from solid solutions or directly on crystallization.

Very clear examples of the dependence of the melting points of the metallic compounds on the positions of the reacting elements in the periodic system are afforded by compounds formed by transition-group metals with nonmetals: boron, silicon, carbon and nitrogen. Compounds of this type belong to a special class of compounds, the majority of which form so-called interstitial phases [18]. These compounds have very high melting points and high hardness, and they all have metallic properties.

In Fig. 6 data are given on the melting points of some compounds formed by these metals with boron (borides), silicon (silicides), carbon (carbides), and nitrogen (nitrides). It will be seen from these data that a general law is observed by the melting points of these compounds: the melting points of these metallic borides, silicides, carbides, and nitrides rise regularly in a given group of elements as the atomic number of the element increases (Fig. 6). For example, chromium boride has a lower melting point than molybdenum boride, and molybdenum boride has a lower melting point than tungsten boride. The carbides of these metals have the highest melting points, the carbides of elements of
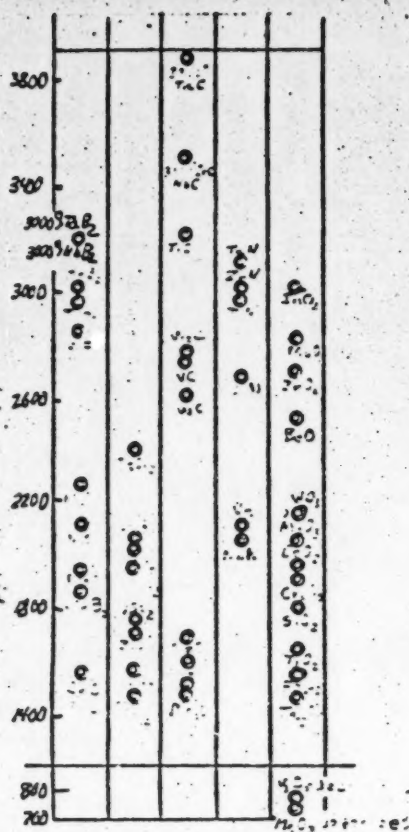

Fig. 6. Melting points of the borides, silicides, carbides, and nitrides of some metals of the transitional groups of the periodic system.

higher atomic number having the higher melting points.

The questions relating to the formation of metallic compounds that we have examined above form part of the general problem of inorganic compounds. As we have shown above, the chemical interactions of metals are characterized by a number of transitional stages: from solid metal solutions to metallic compounds of variable and constant composition, and from these to compounds of the ionic type. This evolution by gradual transition from the metallic type of bond to the ionic type is characterized also by sudden jumps that form a manifestation of the dialectical law of the transition of quantitative changes into a new quality. All this arises from the chemical properties of the elements, which are based on Mendeleev's periodic law.

The solution of these general problems is of great importance for the establishment of the general laws of the formation of solid metal solutions and metallic compounds. These investigations are important also in the study of simple and complex phase diagrams of metal systems. They serve as a basis for the prediction of the types of phase diagram not only of binary, but also of many ternary, quaternary, and more complex metal systems, the great majority of which have not been studied experimentally.

SUMMARY

1. The chemical interaction between metals or between metals and metalloids, which results in the formation of various substances having metallic properties, is characterized essentially by the formation of metallic solutions

and metallic compounds.

2. The chemical resemblances and differences between metallic elements, which are associated with the dispositions of the elements in the same or different groups of the periodic system, are the fundamental factors determining the possibility of the formation of solid metal solutions in some cases and metallic compounds in others.

3. In accord with the teachings of Mendeleev and Kurnakov concerning solutions and compounds, it has been shown that there is a close relationship between metallic solutions and metallic compounds. These two kinds of interaction between metals must be regarded in their essential unity. The fundamental laws of dialectical materialism — the transition of quantitative changes to a new quality, and the unity of opposites — are manifested in graphic form in the transitions of metallic solutions and metallic compounds.

4. The name "metallic compound", first introduced by Kurnakov in 1899, is the most satisfactory designation for those products of the chemical interaction of metals which, their great variety notwithstanding, are distinguished by one fundamental feature, the metallic character of the bond. The name metallic compound" must be substituted for many indefinite foreign terms that were brought into Soviet science without adequate critical examination, e.g. intermetallic compounds, intermediate phases, secondary solid solutions, etc.

5. With the object of gaining the acknowledgement of the priority of Russian science in the discovery of metallic compounds formed as a result of thermal transformations of solid solutions, it is proposed to call them "Kurnakov compounds". since Kurnakov was the first to establish, in 1914, the formation of such compounds in the system gold-copper. a phenomenon that has since been observed in practically all solid metal solutions.

6. With increase in the chemical difference between metallic elements. as deduced from their positions in different groups of Mendeleev's periodic system, the kind of interaction characterizing the formation of solid solutions gradually passes over to the formation of metallic compounds from liquid solutions.

7. The stability or strength of the bond between atoms of different elements in metallic compounds determines the temperature at which the compounds are formed: the more stable the compound, the higher the formation temperature. It has been shown by an examination of some metallic compounds of magnesium, iron and transitional-group metals, that the stability and the formation temperature of a compound rise as the difference in the chemical properties of the elements increases.

8. The laws of formation of metallic solutions and metallic compounds are important for the theoretical determination of the nature of the interaction of metals and the prognosis of the types of phase diagrams that will be found in systems not yet studied. This method of predicting the as yet unstudied phase diagrams of simple and complex metal systems, which is on principle possible, is of great importance, not only for the study of metals now widely employed in practice (iron, nickel, aluminum, etc.), but also for the study of metals forming equilibrium systems that have as yet received little or no study. These metals include chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium, and hafnium.

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LIMITING CURRENTS ASSOCIATED WITH THE CATALYTIC DISCHARGE

OF HYDROGEN IONS IN PRESENCE OF AMINES

COMMUNICATION 2. CATALYTIC EFFECT OF QUININE

S. G. Mairanovsky

In the present paper we give the results of an experimental verification of the theory developed previously [1]. The main subject for investigation has been the catalytic action of quinine in presence of hydrochloric acid as a proton donor. Quinine is one of the most active catalysts [2] and considerably reduces the hydrogen overvoltage: its catalytic wave does not merge with the background even at pH < 1, and can be detected at a quinine concentration of $1 \cdot 10^{-6}$ M.

Hydrochloric acid provides only one kind of proton donor, the concentration of which is readily calculated, but in buffered solutions, which have been used by other authors [3, 4], the phenomena are complicated by the presence of several kinds of donors and by the kinetics of the conversion of one kind into another at the electrode surface [5, 6].

All measurements were carried out in N LiCl as supporting electrolyte. This high concentration of indifferent electrolyte enabled us to neglect changes in the ionic strength of the solution when working with various concentrations of hydrochloric acid.

EXPERIMENTAL

Materials. The quinine used in this work was the monohydrochloride, m p 159°. Its concentration in the original solutions was determined by amperometric titration with hydrochloric acid. The hydrochloric acid ("chemically pure" brand) was used in the form of 0.1 N and 0.5 N solutions, and its polarographic purity was checked by polarography of solutions neutralized with caustic potash ("pure for analysis" brand). In calculating the concentration of hydrochloric acid in the polarographic solutions, a correction was made for the neutralization of the second equivalent of quinine. The lithium chloride (chemically pure" brand) was checked for polarographic purity. Its solutions were not strictly neutral, and the original solution (2N) was therefore neutralized with hydrochloric acid until a just-perceptible hydrogen wave appeared in a polarographic test of the solution (galvanometer sensitivity 10^{-8} amp per division). The remaining reagents used in the work were ammonium chloride, "pure for analysis"; sodium acid hydrosulfide ("chemically pure"; and pyridine base, "chemically pure", distilled.

Apparatus The experiments were carried out on a visual polarograph at $25 \pm 0.2°$. In order to increase the accuracy of readings, the oscillations of the galvanometer were damped by Skobets and Kavetsky's method [7]. The mercury at the bottom of the vessel served as anode. The characteristics of the capillary of the dropping electrode were as follows m = 2.70 mg sec^{-1}, t = sec. $^{2/3}$ $^{1/6}$ = 1.47 mg$^{2/3}$ sec$^{-1/2}$ The values of the limiting currents were not adjusted to $m^{2/3} \cdot t^{1/6} = 1$. The heights of the waves were corrected for residual current. Air was removed from the solutions investigated by passage of hydrogen, which was given a preliminary passage through N LiCl at 25°.

RESULTS OF EXPERIMENTS

A number of polarograms obtained at various quinine and hydrochloric acid concentrations are given in Figures 1 and 2. The abscissae are values of potentials in volts referred to the potential of mercury in N LiCl The values of the potentials are not corrected for the ohmic potential drop in the cell and galvanometer The ordinates are values of current in microamp. It will be seen from Figures 1 and 2 that the polarograms have two waves, the first of which occurs at less negative potentials and corresponds to the catalytic wave, while the second corresponds to the usual discharge of hydrogen ions. The height of the composite wave corresponds to the diffusion current of hydrogen ions.

The results show that at first the limiting catalytic current rises with increase in the quinine concentration; the rate of rise then becomes less, and the current tends to a definite limit. It is not difficult to see that this limit is the value of the hydrogen ion diffusion current $< DH = [DH^+]_0$. The limitation of the growth of the catalytic wave is therefore of a diffusional nature. As the
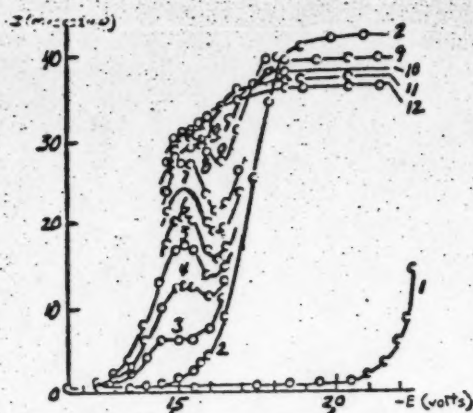

Fig. 1. Catalytic waves in presence of HCl for different concentrations of quinine 1) residual current (N LiCl); 2) 6 8 · 10⁻³ N HCl. 3-12) curves of the catalytic current for rising concentration of quinine.
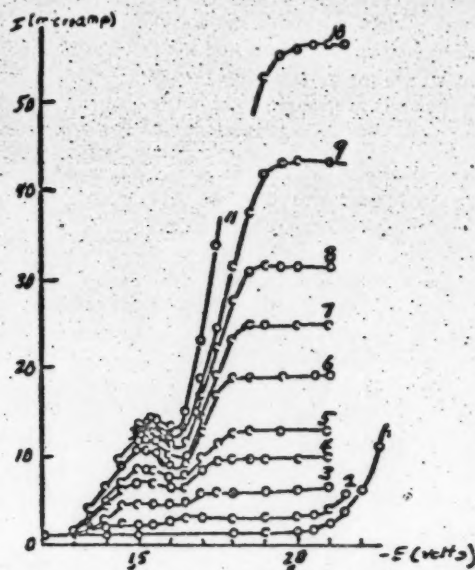
Fig. 2. Catalytic curves produced by quinine at different concentrations of hydrochloric acid: 1) supporting electrolyte (N LiCl; 2-11) acid concentration rises from 2 to 11.

concentration of acid in the solution is increased, the limit to the growth of the catalytic current moves upward.

If, after the limit associated with the diffusional restriction of hydrogen ions has been attained, increase in the quinine concentration continues, then at more negative potentials a new wave (Fig. 3), similar in form to the catalytic wave, makes its appearance. It is possible that this wave is the result of catalytic discharge of hydrogen, in which water molecules serve as proton donors.

Fig. 3. Limiting catalytic current in presence of 0.0 N HCl. a) Polarograms for different quinine concentrations (in 10⁻⁶ M): 1) 0. 2) 3. 5; 3) 7.1; 4) 10.2; 5) 14.2; 6) 17.7; b) dependence of i_{lim} on the quinine concentration.
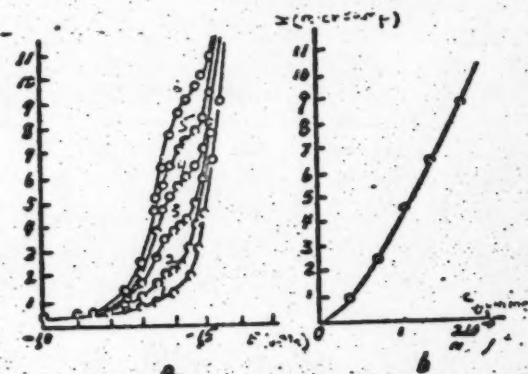
Experiments at Constant Quinine Concentration.   In Fig. 2 are given the polarograms, and in the first columns of Table 2 are presented the experimental results, obtained at different acid concentrations and at approximately constant catalyst concentration.

TABLE 1

Dependence of Limiting Catalytic Current on Quinine Concentration

Concentration Quinine (10^{-5} M)	HCl (10^{-3} M)	i* expt. (microamp)	$\kappa_{DH^+}[DH^+]_0$ (microamp)	i calcd. (microamp)	Concentration Quinine (10^{-5} M)	HCl (10^{-3} M)	i expt. (microamp)	$\kappa_{DH^+}[DH^+]_0$ (microamp)	i calcd. (microamp)
1.36	3.65	4.2	22.3	4.34	1.41	6.78	5.42	41.3	5 32
2.72	3.63	8.5	22.1	7.92	3.10	6.71	11.6	40.9	12.3
4.06	3.59	11.4	21.9	11.1	4.43	6.69	16.3	40.7	16.5
5.40	3.57	12.5	21.8	13.0	6.34	6.64	19.4	40.4	20.7
6 70	3.53	14.5	21.6	14.2	8.50	6.55	24.0	39.9	24.0
9.30	3.48	15.6	21.2	15.7	11.1	6.47	26.3	39.4	26.6
11.8	3.42	16.3	20.9	16.5	16.5	6.29	29.1	38.3	29.4
14.3	3.37	16.8	20.5	16.9	21.5	6.13	29.8	37.4	30.2
28.0	3.28	17.0	20.0	17.1	26.5	5.98	30.6	36.5	31.1
31.6	3.21	17.1	19.6	17.3	36.0	5.74	31.8	35.0	31.3

*i is the limiting catalytic current

The results show that at first the catalytic current increases proportionally to the rise in acid concentration; the rate of increase then becomes less, and finally, at a sufficiently high acid concentration, the current tends to a limit determined by the catalyst concentration. The higher the concentration of catalyst the higher the limiting catalytic current and the higher the acid concentration required for its attainment. As the limit to the rise in catalytic current occurs at relatively high acid concentrations, it may be supposed that this limit is associated with the filling of the electrode surface with hydroxonium ions, which do not succeed in becoming catalytically discharged at low quinine concentrations.

TABLE 2

Dependence of the Limiting Catalytic Current on the Acid Concentration

Concentration Quinine (10^{-5} M)	HCl (10^{-3} M)	i* expt. (microamp)	b (liter/mmole)	i calcd. (microamp)	Concentration HCl (10^{-3} M)	Quinine (10^{-5} M)	i expt. (microamp)	b (liter/mmole)	i calcd. (microamp)
0.47	3.30	1.12	3.0	1.36	0.46	7.90	1.59	2.9	1.75
0.95	3.29	3.74	1.0	3.83	1.09	7.86	4.4	0.76	4.57
1.45	3.27	5.6	0.54	5.36	3.09	7.70	13.4	0.71	13.4
1.93	3.26	7.2	0.44	6.57	4.50	7.60	18.5	0.61	17.7
2.90	3.23	8.9	0.62	8.50	5.96	7.48	22.1	0.62	21.4
3.93	3.20	10.4	0.64	10.0	7.46	7.37	22.4	0.85	24.3
4.96	3.14	11.5	0.64	11.1	8.95	7.23	25.6	0.76	26.9
6.93	3.10	12.7	0.67	12.5	10.2	7.12	26.9	0.77	28.3
9.12	3.05	13.3	0.71	13.3	11.5	7.03	28.4	0.75	29.5
16.8	2.78	13.3	0.78	14.25	14.1	6.85	30.1	0.76	31.4
-	-	-	-	-	26.5	6.66	30.7	0.77	32.6
-	-	-	-	-	23.0	6.15	30.5	0.80	33.6

Experiments in Presence of 0.05 N HCl. In Fig. 4 a polarograms obtained in presence of 0.05 N HCl are given, and in Fig. 4 b the points show the dependence of the limiting catalytic current on the quinine concentration. The form of this curve is somewhat unusual: it is convex with respect to the axis of abscissas. Its slope falls with increase in the concentration of catalyst, falling to zero at sufficiently high concentrations, so that the curve becomes a straight line. This kind of relationship between the current and the catalyst concentration may be observed also for other amines as can be seen from Kirkpatrick's graphs [3]; Kirkpatrick, however, attached no importance to this phenomenon and does not mention it in the text.

Fig. 3 Appearance of a second catalytic wave due to quinine [quinine concentration c_q in 10^{-4} M, HCl concentration (c_{HCl}) in 10^{-3} M; 1) c_q = c_{HCl} = 3.07; 2) c_q = 1.1, c_{HCl} = 3.1; 3) c_q = 1.97, c_{HCl} = 2.57; 4) c_q = 2.53, c_{HCl} = 2.82; 5) c_q = 3.0, c_{HCl} = 2.0; 6) c_q = 4.67, c_{HCl} = 2.30; 7) c_q = 5.64, c_{HCl} = 2.14; 8) c_q = 7.36, c_{HCl} = 1.78

DISCUSSION OF RESULTS

The equations that we have introduced are in agreement with the experimental results obtained at various quinine and hydrochloric acid concentrations. The experimental results enable us to evaluate the constants occurring in these equations.

Experiments at High Acid Concentration. From Equations 30 and 31 of the previous communication [1]* it follows that

$$rp = 2 / \kappa_g \qquad (44)$$

Assuming that κ_g = 2.33 microamp·mmole/liter, as found from data on the electrical conductivity of quinine [8], we obtain the value of 0.86 mmoles/microamp-liter for rp. Substitution of the value of rp and experimental values of i and $[K]_g$ (Fig. 4) in Equation 41 yields several systems of equations. Solution of these systems gives Q^2 = 1030 microamp liter/mmole for $[DH]_o^+$ = 50 mmoles/liter) and χ = 1.1 · 10^{-5} mmoles/liter. Equation 44 gives the value 7.8 · 10^{-4} microamp^{-1}.

These values of the constants were used in constructing the theoretical curve $i = f [K]_g$ from Equation 42. The curve is shown in Fig. 4 b.

The character of the dependence of the current on the quinine concentration at low values of the latter may be explained on the basis of the mechanism discussed in the first communication [1] for the formation of the catalytic current. At very low catalyst concentrations the slowest stage is the process III, the interaction of uncharged complexes [1]. Owing to the slow rate at which they interact and their comparatively high rate of formation, the proportion of uncharged complexes in the total surface concentration of catalyst may be fairly high. These complexes form the passive part of the surface concentration of catalyst, taking no direct part in the catalytic process. The rate at which the passive part of the catalyst is converted into active catalyst, i.e., the rate of the interaction of the complexes depends on the square of the surface concentration of these complexes. This rate is also essentially determined by the value of the catalytic current at very low values of $[K]_g$. As the concentration of catalyst increases, the rate of interaction of the complexes increases more rapidly than their rate of formation, and the proportion of them in the total surface concentration rapidly falls. As a result, the slowest stage, determining the value of the catalytic current, becomes the direct process (7), the rate of which varies linearly with the active part of the surface concentration of catalyst. Further increase in the concentration of the catalyst lowers the proportion of passive catalyst to such an extent that it may now be neglected in comparison with the total surface concentration. In this case the relationship between the catalytic current and the catalyst concentration becomes a linear one (with a proportionality coefficient of Q').

Dependence of the Limiting Current on the Acid Concentration. The dependence of limiting currents on proton-donor concentrations is shown in Fig. 5. The points correspond to the experimental values of the current (see Table 2). For the catalytic waves the points are extrapolated linearly to the same concentration of quinine. The values of currents lying on the straight line correspond to the height of the composite wave, i.e. to the value of the hydrogen diffusion current. The slope of the straight line gives the value κ_{DH} = 6.1 microamp liter/mmole for hydrochloric acid in N LiCl ($m^{2/3} t^{1/6}$ = 1.47 $mg^{2/3}$ sec$^{-1/2}$). The assemblies of points along the curves give the experimentally found dependence of the catalytic current on the hydrochloric acid concentration. Theoretically, this relationship is given by Equation 33, which represents the observed facts fairly well.

At a sufficiently low concentration of proton donor, the curve for the limiting catalytic current practically coincides with the straight line representing the dependence of the diffusional, noncatalytic current due to hydrogen-ion discharge on the donor concentration (Fig. 5).

It is not difficult to see that the field of donor concentrations within which the two lines become coincident grows as the catalyst concentration rises. The explanation of this is that at low donor concentration all the particles

* The numbering of the equations is the same for both communications.

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of donor that reach the electrode surface are "dealt with" by the catalyst. It is obvious that the higher the concentration of catalyst, the greater will be the amount of donor that it can "deal with" completely. As the content of donor in the solution is increased, the value of the catalytic current becomes less than the total current due to the discharge of hydrogen ions. This means that the catalyst will no longer be able to "deal with" the whole of the donor that arrives at the electrode. With further increase in donor concentration, the rate of rise of the catalytic current will become lower and lower, and will tend to some limiting value determined by the concentration of the catalyst and its capacity for dealing with donor. Equation 33 is transformed, first into Equation 37, and, finally, with further increase in the concentration [DH+] into Equation 34.

The donor concentration at which the limit of rise of the catalytic current is practically attained is determined by the value of the coefficient b. The value of b can be determined from the experimental data by substituting them in Equation 33. For this purpose it is convenient to modify Equation 33 to some extent. Let us write

$$\vartheta \ K_1{}^2 B^3 DH^{+3} F = R \tag{45}$$

Taking Equation 40 into account, we obtain

$$i = \frac{\kappa_{DH+} [DH^+]_0 \ R \ ([K]_0 - r \quad ip)}{\kappa_{DH+} \ (1 + b \ [DH^+]_0) + R ([K]_0 - r \quad ip)} \tag{46}$$

and from Equation 46 we obtain

$$b = \frac{r([K]_0 - r \quad ip) \ (\kappa_{DH+} \ [DH^+]_0 - i) - \kappa_{DH+}}{\kappa_{DH+} [DH^+]_0 \cdot i} \tag{47}$$

Fig. 5. Dependence of limiting currents on the concentration of hydrochloric acid: 1 and 2 — catalytic currents at quinine concentrations of $3.3 \cdot 10^{-5}$M and $7.9 \cdot 10^{-5}$M respectively; 3 — diffusion current of hydrogen discharge

When the experimental values given in Table 2 were substituted in Equation 47, a series of equations was obtained which permitted the values of b and R to be found. The values of b and R so found were not strictly constant: they varied within certain limits according to the acid/quinine concentration ratio.
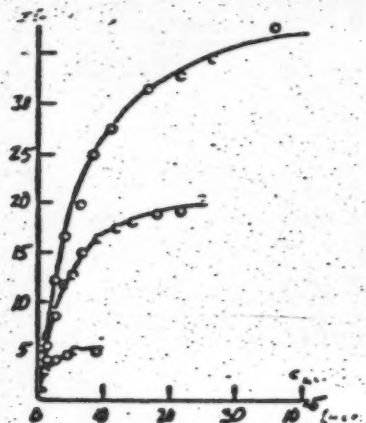
We may assume, for simplicity, that the discrepancies in the values of b and R, determined from Equation 47, are due to the variable nature of b. Substituting the mean value of b (0.7 liter/mmole) and the value $Q' = 1030$ microamp·liter/mmole (in 0.05 N HCl) in Equation 39, and applying also Equations 36 and 45, we find that $Q = 1060$ microamp.liter/mmole and $R = 740$ microamp·liter^2/mmole^2. The value of R was substituted in Equation 47, and from the experimental data a series of values of b for various values of $[DH^+]_0/[K]_0$ was found. These values are given in the fourth column of Table 2. At relatively high and low concentrations the value of b is somewhat higher than at moderate concentrations, where it is approximately constant. The increase in the value of b arises from the fact that the value of the catalytic current is lower than that derived from our equations.

The lowering of the value of the catalytic current at very low acid concentrations may be explained as follows. Apart from diffusional restrictions, which are taken into account in the derivation of the equations by means of the constant κ_{DH+}, in the case of a catalytic process there is a further

Fig. 6. Dependence of the limiting catalytic current on the quinine concentration; hydrochloric acid concentrations in 10^{-3}M: 1 — 1.06; 2 — 3.65; 3 — 6.8

...ding factor. The essential point is that it is not sufficient for the proton donor to come to the electrode surface, it must then move a certain distance over the surface until it meets a catalyst molecule. The effect of such sliding about" will be particularly notable at low donor concentrations, when the slowest stage, which determines the value of the catalytic current, is the supply of proton donors to the catalyst. As the concentration of donor increases, the slowest stage becomes the action of the catalyst on the donor, and the effect of sliding becomes inappreciable.

A certain rise in the value of b at high acid concentrations may be explained by the fact that in this case each catalyst molecule has to deal with close to the maximum amount of donor and therefore causes the evolution of a large amount of molecular hydrogen, which, not being able to escape sufficiently rapidly from the electrode, hinders the approach of donor to catalyst.

The last column of Table 2 contains values of limiting currents calculated by Equation 46 by substitution of $R = 740$ microamp $\cdot$ liter^2/mmole^2 and $b = 0.7$ liter/mmole. At the same time, in order to avoid cumbersome calculations, a rounded value of the experimental current was placed under the root sign in Equation 46. It will be seen, by a comparison of values of the current calculated and found experimentally, that the discrepancies between them, in spite of the great variation on the value of b, are comparatively small. Exceptions are formed by values of currents at low acid concentration.

Dependence of the Value of the Limiting Current on the Catalyst Concentration. The variation of the limiting current with the quinine concentration is shown in Fig. 6. The points correspond to experimental values (Table 1) linearly extrapolated to the same acid concentration. It will be seen from the figure that, as the quinine concentration increases, the current tends to a definite limit, which, as already pointed out, is determined by the rate at which hydrogen ions are presented to catalyst molecules at the electrode surface. This same inference follows from analysis of Equation 46. As the concentration of the catalyst is increased, the second term of the denominator of the expression in Equation 46 increases, so that, when a certain concentration of quinine is attained, the value of the first term can be neglected in comparison with the second, and Equation 46 becomes $i = \kappa_{DH^+}$ [DH$^+$].

The calculated values of the currents (last column, Table 1) agree with those found experimentally. The curves presented in Fig. 6 are constructed from Equation 46 ($R = 740$ microamp liter^2/mmole^2 and $b = 0.7$ liter/mmole). The experimental points fit very well to these curves.

Determination of the Value of the Catalytic Current. Calculation shows that, if for the catalytic current we take not the value i_m, but its true value i_1 (see Fig. 1 of the previous communication [1]), then the variation in the value of b (for a corresponding value of R) is greatly reduced, and the agreement between calculated and experimental values of the current is very much improved. Fairly good agreement between calculated and found values of the current is found also when the value i_{mean}, at the middle of the section of the catalytic wave between the maximum and minimum, is taken as the value of the limiting catalytic current. As will be seen from Fig. 1 of the previous communication [1], at a potential corresponding to i_{mean}, the wave has almost attained its maximum, whereas the rise in wave 3 has not yet set in, the current being that corresponding to a "pure" catalytic wave.

The value of i_{mean} is readily measured in practice, and it may therefore be used for analytical purposes, whereas for the determination of i_1 it is necessary to obtain the whole polarographic curve and carry out cumbersome calculations. It is thus expedient to take the value i_{mean} as the value of the catalytic current.

Evaluation of the Reaction-rate Constants. From the numerical values of the overall constants we may calculate certain quantities that are involved in them. By use of the values

$$R = 740 \text{ microamp} \cdot \text{liter}^2/\text{mmole}^2 = 740 \text{ amp} \cdot \text{liter}^2/\text{mole}^2 \text{ and } S = 3.38 \cdot 10^{-3} \text{ sq. cm}$$

we obtain

$$k_2 a_B a_{DH^+} = 2.0 \text{ liter}^2/\text{cm}^2 \cdot \text{mole} \cdot \text{sec}$$

For uncharged particles, such as B and BH, we may take a_B as the thickness of the electrode surface layer [9], equal to about $1 \cdot 10^{-18}$ liter/cm^2. The value of a_{DH^+} for hydroxonium ions on the cathode must be greater by a

factor of several powers of ten. Its value can be estimated as follows. According to Equations 4 and 6:

$$a_{DH^+} = \frac{a_{DH^+}}{1 + b[DH^+]_0} = \frac{[DH^+]_s}{[DH^+]_0}$$

$$a_{DH^+} = [DH^+]_s \frac{1 + b[DH^+]_0}{[DH^+]_0}. \tag{48}$$

When the concentration of acid in the solution is very high and we may assume that the electrode surface is saturated with hydroxonium ions, Equation 48 takes the form:

$$a_{DH^+} = [DH^+]_s \text{ lim} \cdot b. \tag{49}$$

Here, $[DH^+]_s$ lim is the limiting surface concentration of hydroxonium ions. If it is assumed that the area occupied by a hydroxonium ion on the electrode surface is about 10 $(\text{Å})^2$, then

$$[DH^+]_s \text{ lim} \approx 1 \cdot 10^{15} : 6 \cdot 10^{23} \approx 1.6 \cdot 10^{-9} \text{ mole/cm}^2$$

and a_{DH^+} is about $5 \cdot 10^{-7}$ liter/cm². The value of k_1 is therefore of the order of $4 \cdot 10^{16}$ cm²/mole. sec.

The value of the constant k_3 can be obtained from Equation 31.

Using the value $p = 7.8 \cdot 10^4$ microamp^{-1} and assuming that $\kappa_{BH} = \kappa_B = 2.33$ microamp · liter/mmole, we find that $k_3 a_{BH}^2 = 3 \cdot 10^2$ liter²/cm². mole. sec.

If we assume that $a_{BH} = a_B = 1 \cdot 10^{-19}$ liter/cm², then the value of k_3 will be of the order of $3 \cdot 10^{22}$ cm²/mole.sec.

Thus, the constant for the rate of formation of a hydrogen molecule from complexes of quinine with H atoms is about 10^5 times as great as the rate constant for the interaction of quinine with the hydroxonium ion.

As is shown by the results of our experiments with other proton donors (e.g., NH_4^+) and various catalysts (semicarbazide, pyridine), and also by the results of the authors cited [2, 3, 4], the relation observed between the limiting currents and the composition of the solution is similar in all cases to that found in catalysis with quinine. We may therefore suppose that the hypotheses advanced here are reflections of general laws applying to the catalytic current at a dropping mercury electrode.

I take this opportunity of expressing my great indebtedness to Prof. M. B. Neiman for constant interest in the work.

SUMMARY

1. The previously deduced equations [1] have been verified quantitatively for the catalytic system quinine—hydrochloric acid.

2. The experimental results show that the rate constant for the formation of hydrogen molecules from quinine—hydrogen atom complexes is about 10^6 times as great as the rate constant for the interaction of quinine and hydroxonium ions.

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HETEROGENEOUS EQUILIBRIA IN THE SYSTEMS

$LiCl - RbCl - H_2O$ AND $LiCl - CsCl - H_2O$

V. P. Blidin

There are no data in the literature concerning the solubility relations in aqueous systems containing both lithium chloride (a salt of one of the lightest Group I metals) and rubidium or cesium chloride (salts of the heaviest known alkali metals). The investigation of the chemical interactions of these components in aqueous solutions is of theoretical and practical interest.

It is well known that lithium compounds accompany rubidium and cesium compounds in minerals, soils, and natural waters of various origins, the concentrations of all these compounds being generally quite small. Lithium chloride gives hydrated double salts with many bivalent-metal chlorides: Voskresenskaya and Yanatyeva [1] who studied the system $LiCl - MgCl_2 - H_2O$, obtained a salt of composition $LiCl \cdot MgCl_2 \cdot 7H_2O$; Basset and Sandersen [2], investigating the system $LiCl - CoCl_2 - 2H_2O$, found several double salts, such as $LiCl \cdot CoCl_2 \cdot 2H_2O$, $7LiCl \cdot 2CoCl_2 \cdot 18H_2O$, and $3LiCl \cdot 2CoCl_2 \cdot 6H_2O$, together with solid solutions over certain concentration ranges; and Benraht [3, 4] showed that $LiCl$ formed similar types of double salts with nickel, manganese, and copper chlorides.

The study of these systems is of interest also because rubidium and cesium chlorides resemble lithium chloride in forming double salts of the same type with salts of the same metals. Thus, in hydrochloric acid solution they form double salts with the chlorides of copper, iron, zinc, cadmium, and manganese. From aqueous solutions containing cobalt chloride, beautiful dark-blue and lilac prismatic crystals separate, and these include the compounds $CoCl_2 \cdot RbCl \cdot 2H_2O$, $CoCl_2 \cdot 2RbCl \cdot 2H_2O$, $CoCl_2 \cdot CsCl \cdot 2H_2O$, $CoCl_2 \cdot 2CsCl \cdot 2H_2O$, $CoCl_2 \cdot 3CsCl \cdot 2H_2O$ [5] Rubidium and cesium carnallites $RbCl \cdot MgCl_2 \cdot 6H_2O$ and $CsCl \cdot MgCl_2 \cdot 6H_2O$, the analogs of $LiCl \cdot MgCl_2 \cdot 7H_2O$, are found in nature. On the other hand, no hydrated double salts could be detected by Novoselova and Sosnovskaya [6] in the system $LiCl - BeCl_2 - H_2O$, nor by Blidin [7] in systems containing lithium chloride together with chlorides of calcium, strontium, and barium.

EXPERIMENTAL

Preparation of the Starting Substances; Methods of Chemical Analysis and Investigation

Lithium chloride was prepared from pure lithium carbonate by dissolving it in chemically pure hydrochloric acid. The dried product was dissolved in alcohol, and the solution was evaporated down on a water bath until crystals of lithium chloride formed. The rubidium and cesium salts were recrystallized and then checked analytically; the results obtained corresponded to chemically pure substances.

Chlorine was determined both gravimetrically and by Mohr titration with 0.01 N $AgNO_3$. Rubidium and cesium were determined as chloroplatinates, the same precipitation conditions being observed as in the determination of potassium. Lithium was determined by difference from the total amount of chlorides.

In order that our results concerning the behavior of the components should be as reliable as possible, we investigated the isotherms at 25° and 40°. The solubility investigations were carried out in an electrically heated water thermostat, in which the temperature was maintained constant within ± 0.1° by means of a toluene thermoregulator. The determination of the solubility of lithium chloride was carried out in a reaction vessel having an oil seal, increasing amounts of rubidium or cesium chloride being added; or alternatively, a saturated solution of the rubidium or cesium salt was taken, and increasing amounts of lithium chloride were added.

The solutions were agitated with a glass stirrer driven by an electric motor. The mixtures were stirred at constant temperature until equilibrium between liquid and solid phases had been established, which generally required 6-8 hours, as indicated by the results of chemical analyses on a number of test samples. After the mixture

had settled in the reaction vessel, a sample (0.3-0.5 g) of the liquid phase was removed by pipet and transferred to two weighed weighing bottles. The weighed samples were dissolved in 100 ml measuring flasks, and then separately analyzed for chlorine and rubidium or cesium.

Solid phase was removed in a finely perforated silver spoon, which served as a filter, and the analysis was performed exactly as for the liquid phase. The compositions of the solid phases were determined by the Schreinemakers residue method [5]. The solubility results were plotted on Roozeboom triangles, compositions being expressed in the diagrams in percent by weight.

25° and 40° Isotherms for the System LiCl – RbCl – H₂O.

In the investigation of this system, and also of the system LiCl – CsCl – H₂O, it was found that as the amount of RbCl (or CsCl) added to a saturated solution of LiCl was increased, the viscosity of the solution increased until the pure components separated out into the solid phase. The analytical data for the isotherms are given in Tables 1 and 2 and represented in the diagrams (Figs.1 and 2).

The 25° and 40° isotherms have four sections, and there are four solid phases: LiCl · H₂O, RbCl · 2LiCl · 4H₂O, 3RbCl · LiCl · 2H₂O and RbCl.

Thus our investigations have led to the detection of two types of compounds in this system: RbCl·2LiCl·4H₂O, and 3RbCl · LiCl · 2H₂O. The compound of the first type, which has a greater solubility than the original components, forms tabular crystals in rosettelike clusters (Fig. 3).

TABLE 1

25° Solubility Isotherms for the System LiCl – RbCl – H₂O.

Point No.	Amount (% by wt.)			ε of salts	Composition of solid phase (% by wt.) *		Solid phase
	LiCl	RbCl	H₂O		LiCl	RbCl	
1	45.95	–	54.05	45.95	–	–	LiCl · H₂O
2	43.50	6.47	50.03	49.97	54.31	3.62	
3	41.17	11.63	47.20	52.80	52.04	6.70	
4	40.52	15.86	43.62	56.38	–	–	LiCl · H₂O + RbCl · 2LiCl · 4H₂O, point B
5	39.05	16.92	44.03	55.97	35.63	28.72	
6	32.90	21.56	44.54	55.46	32.20	31.13	RbCl · 2LiCl · 4H₂O
7	30.44	24.17	45.39	54.61	31.26	31.24	
8	29.08	25.21	45.71	54.29	–	–	RbCl · 2LiCl · 4H₂O + 3RbCl · LiCl · 2H₂O, point C
9	28.51	21.60	49.89	50.11	17.48	56.03	
10	26.65	19.52	53.83	46.17	15.64	58.15	
11	23.26	20.04	56.70	43.30	24.13	59.27	
12	19.30	21.48	59.22	40.78	13.07	61.02	3RbCl · LiCl · 2H₂O
13	12.98	27.45	59.57	40.43	10.10	64.78	
14	8.60	35.09	56.31	43.69	7.84	67.50	
15	6.75	39.87	53.38	46.62	–	–	3RbCl · LiCl · 2H₂O + RbCl, point D
16	5.34	41.55	53.11	46.89	3.25	79.12	
17	2.60	44.17	53.23	46.77	1.68	81.53	RbCl
18	–	48.12	51.88	48.12	–	–	

The compound of the second type 3RbCl · LiCl · 2H₂O was similar in external habit to crystals of rhombic syngony (Fig. 4). The compound RbCl · 2LiCl · 4H₂O was less hygroscopic than LiCl; unlike the compound 3RbCl · LiCl · 2H₂O, which is practically unaffected by a mixture of ether and alcohol, it is decomposed by this mixture.

In order to verify the compositions of the compounds obtained we prepared synthetic solutions corresponding to the compounds, placed these in vessels, and evaporated them isothermally under reduced pressure. The crystals obtained were rapidly pressed between filter papers, and dried in a desiccator over sulfuric acid, the crystals being spread out on a thick layer of filter papers, which gradually imbibed the part of the mother liquor that was not removed by simple pressing. Analysis of the crystals gave the following results:

Found %: RbCl 42.86; LiCl 30.24; H₂O 26.90

RbCl · 2LiCl · 4H₂O Calculated %: RbCl 43.54; LiCl 30.53; H₂O 25.93

Found %: RbCl 81.64; LiCl 9.94; H₂O 8.42

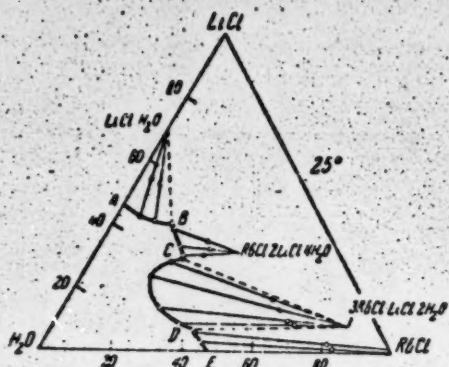3RbCl · LiCl · 2H₂O Calculated %: RbCl 82.23; LiCl 9.61; H₂O 8.16
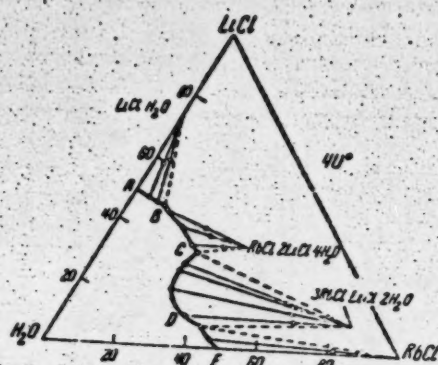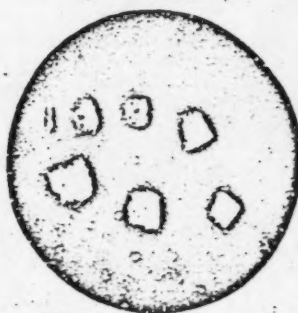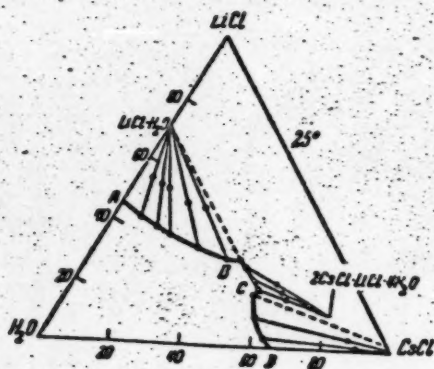
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 7.

Fig. 5.

Fig. 6.

TABLE 2
40° Solubility Isotherm for the System LiCl –RbCl –H₂O

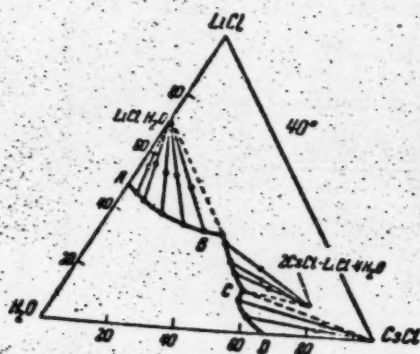| Point No.	Amount (% by wt.)			ε of salts	Composition of solid phase (% by wt.)		Solid phase
	LiCl	RbCl	H₂O		LiCl	RbCl	
1	47.98	–	52.02	47.98	–	–	
2	46.68	3.47	49.85	50.15	58.72	1.68	LiCl · H₂O
3	45.74	7.26	47.00	53.0	59.53	3.40	
4	45.13	9.51	45.36	54.64	–	–	LiCl · H₂O + RbCl · 2LiCl · 4H₂O, point B
5	44.05	10.48	45.47	54.53	39.10	24.38	
6	38.02	18.24	43.74	56.26	36.05	27.12	RbCl · 2LiCl · 4H₂O
7	32.51	24.60	42.89	57.11	32.70	32.96	
8	30.22	27.14	42.64	57.36	–	–	RbCl · 2LiCl · 4H₂O + 3RbCl · LiCl · 2H₂O, point C
9	26.44	25.46	48.10	51.90	15.86	60.04	
10	24.43	25.17	50.40	49.60	14.34	62.12	
11	21.26	25.03	53.71	46.29	14.10	63.20	
12	18.45	25.66	55.89	44.11	11.82	63.47	3RbCl · LiCl · 2H₂O
13	15.50	28.74	55.76	44.24	9.53	65.61	
14	9.78	34.63	55.59	44.41	8.20	65.59	
15	7.34	40.12	52.54	47.46	–	–	3RbCl · LiCl · 2H₂O + RbCl, point D
16	2.50	45.26	52.24	47.76	1.50	80.83	RbCl
17	–	49.85	50.15	–	–	–	

TABLE 3
25° Solubility Isotherms for the System LiCl –CsCl –H₂O

Point No.	Amount (% by wt.)			ε of salts	Composition of solid phase (% by wt.)		Solid phase
	LiCl	CsCl	H₂O		LiCl	CsCl	
1	45.95	–	54.05	45.95	–	–	
2	42.24	5.52	52.24	47.75	55.04	2.46	
3	39.76	11.48	48.76	51.24	53.50	6.14	LiCl · H₂O
4	36.38	16.54	47.02	52.92	52.09	8.97	
5	32.63	26.47	36.90	63.10	74.23	16.12	
6	29.81	36.71	33.48	66.52	46.92	21.50	
7	29.03	40.65	30.32	69.68	–	–	LiCl · H₂O + 2CsCl · LiCl · 4H₂O, point B
8	26.38	44.26	29.36	70.64	21.30	55.68	
9	21.48	47.65	30.87	69.13	17.05	60.03	2CsCl · LiCl · 4H₂O
10	18.24	49.84	31.92	68.08	15.02	61.48	
11	15.86	51.92	32.22	67.78	–	–	2CsCl · LiCl · 4H₂O + CsCl, point C
12	10.12	55.63	34.25	65.75	4.76	84.90	
13	3.50	61.48	35.02	64.98	1.57	89.07	CsCl
14	–	65.51	34.49	65.51	–	–	

The compositions at the multiple points on the isotherms, both in this system and in the LiCl –CsCl –H₂O system, are given in relevant tables (see points B, C, and D). These junction points were determined by interpolation (by the intersection of two curves).

The 25° and 40° solubility isotherms have three sections, and there are three solid phases: LiCl · H₂O, 2CsCl · LiCl · 4H₂O and CsCl. The compound 2CsCl · LiCl · 4H₂O, which had a marked monoclinic habit (Fig. 7), was more soluble than its components.

This compound is hygroscopic, though less so than LiCl. It is decomposed by a mixture of ether and alcohol

TABLE 4

40° Solubility isotherms for the System LiCl–CsCl–H$_2$O.

Point No.	Amount (% by wt.) LiCl	CsCl	H$_2$O	c of salts	Composition of solid phase (% by wt.) LiCl	CsCl	Solid phase
1	47.98	–	52.02	47.98	–	–	LiCl · H$_2$O
2	46.04	3.91	30.05	49.95	55.53	2.46	
3	43.75	7.46	48.79	51.21	56.86	4.13	
4	40.02	14.63	45.35	54.65	54.42	8.01	
5	37.56	23.34	39.10	70.90	53.68	11.67	
6	35.71	30.12	34.17	65.83	51.06	17.81	
7	33.62	37.05	29.33	70.67	–	–	LiCl · H$_2$O + 2CsCl · LiCl · 4H$_2$O point B
8	30.73	39.97	29.30	70.70	23.07	53.48	2CsCl · LiCl · 4H$_2$O
9	24.49	45.83	29.68	70.32	19.93	55.88	
10	19.80	48.65	31.55	68.45	15.81	59.40	
11	15.67	52.24	32.02	67.91	–	–	CsCl + 2CsCl · LiCl · 4H$_2$O, point C
12	12.46	53.68	33.86	66.14	4.61	82.45	CsCl
13	6.50	58.76	34.74	65.26	3.13	81.69	
14	–	67.40	32.60	67.40	–	–	

with separation of fine CsCl crystals. The analytical results for the 2CsCl · LiCl · 4H$_2$O crystals were:

Found %: CsCl 75.16; LiCl 9.52; H$_2$O 15.32
Calculated %: CsCl 74.64; LiCl 9.39; H$_2$O 15.96.

It should be noted that as CsCl was added to a saturated solution of LiCl the viscosity of the solution increased, and at the points at which compounds were formed noticeable passage of solid phase into solution occurred.

SUMMARY

1. The 25° and 40° solubility isotherms have been determined for the systems LiCl–RbCl–H$_2$O and LiCl–CsCl–H$_2$O.

2. The compounds RbCl · 2LiCl · 4H$_2$O and 3RbCl · LiCl · 2H$_2$O have been found in the first system, and the compound 2CsCl · LiCl · 4H$_2$O has been found in the second system.

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* See Consultants Bureau Translation, page, 893.

CONDENSATION REACTIONS OF 3-CAMPHENILANECARBOXALDEHYDE

WITH KETONES AND ESTERS

B. A. Arbuzov and L. A. Mukhamedova

The preparation of 3-camphenilanecarboxaldehyde (I) by the isomerization of camphene oxide [1] has made this aldehyde comparatively accessible for use in various syntheses. In this paper we describe our results on condensation reactions of 3-camphenilanecarboxaldehyde with various ketones, with ethyl acetate, and with ethyl acetoacetate. The condensation product of 3-camphenilanecarboxaldehyde with acetone (II) is an isomer of the a- and β-ionones (III and IIIa):
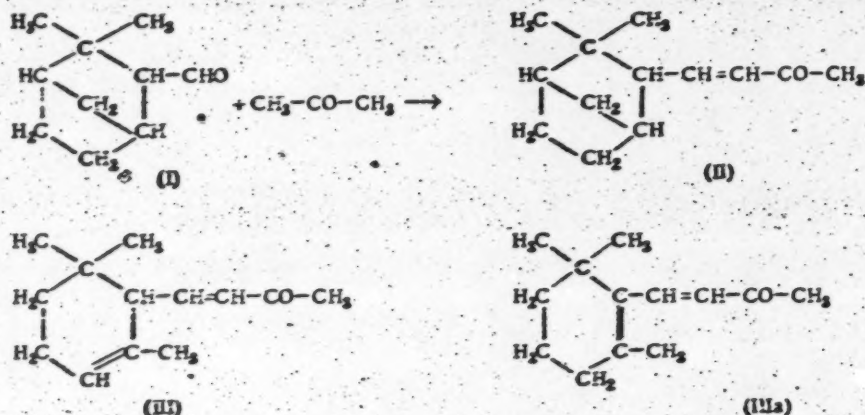
It differs from them in having an endomethylene bridge, formed at the expense of the disappearance of a double bond. It was of interest to determine the effect of this change of structure on the odor, and with this objective syntheses were carried out of the isomer of the ionones, the ketone II, and also of a number of its homologs and analogs *.

When 3-camphenilanecarboxaldehyde was condensed with acetone in presence of sodium ethoxide as condensing agent, complete resinification occurred. In presence of aqueous alkali, however, a product having b.p. 139-140° (12 mm); n_D^{29} 1.5030; d_4^{29} 0.9705, was obtained; it had a feeble camphorlike odor. Analysis of this substance gave a low value (by 1%) for carbon, which may be explained by the presence of some of the corresponding aldol.

When, in fact, the product was distilled with camphorsulfonic acid, a substance was obtained which analyzed as $C_{13}H_{20}O$ and had the following constants: b.p. 136-137° (11.5 mm); n_D^{28} 1.5038; d_4^{28} 0.9692; found MR 58.69; calculated for $C_{13}H_{20}O$, MR 57.38, exaltation 1.31. The ketone so obtained (II) was a pale greenish yellow oily liquid having an odor similar to that of ionone. With semicarbazide it yielded a semicarbazone of m.p. 176-177°. The ketone was obtained in 43% yield.

Khusnutdinov gave the following constants for this ketone: b.p. 137-139° (14 mm); n_D^{28} 1.5507; d_4^{28} 0.9721; MR_D 58.20; semicarbazone, m.p. 164-165°. Khusnutdinov's preparation was evidently not free from the aldol.

The condensation of 3-camphenilanecarboxaldehyde with 2-butanone in an alkaline medium went readily, both in presence of aqueous alkali, and in presence of sodium ethylate, the yields of pure product being practically the same in both cases (30% and 33%, respectively). In both cases the same condensation product was obtained and a small amount of the aldol form was present. Distillation of the product over camphorsulfonic acid

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* Similar work was carried out in our laboratory in 1938-1940 by B. Sh. Khusnutdinov. B. Sh. Khusnutdinov was killed in the Great Patriotic War, defending his Fatherland, and he left only a few constants of the compounds he had prepared [2] The descriptions of the experiments and of the experimental conditions have not been preserved. The work therefore had to be done again.

. . . abled us to isolate it in the pure state, when it corresponded in composition to $C_{14}H_{20}O$ and had the following constants: b.p. 142-144° (12 min), n_D^{20} 1.5000; d_4^{20} 0.9632; Found MR 62.99, Calculated for $C_{14}H_{20}O$ F MR 62.00; exaltation 0.99. The ketone was an oily liquid having an odor similar to that of ionone. Khusnutdinov gave the following constants for this ketone: b.p. 139-140° (12 min); d_4^{20} 0.9608; n_D^{20} 1.4980; MR 62.90; semicarbazone, m.p. 200-201°.

The condensation reaction of 3-camphenilanecarboxaldehyde with 2-butanone can give two products (IV and IVa):
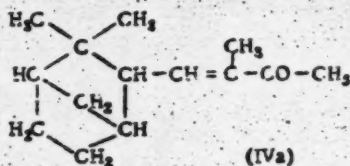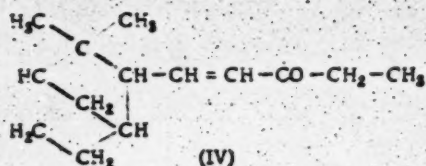

According to the literature [3], the course, of the condensation reaction of aldehydes with acetone homologs depends on the nature of the condensing agent used: when condensation occurs in an acid medium, it is the a-methylene group that takes part, whereas in an alkaline medium condensation will occur with an a-methyl group. These investigations indicate that our ketone should be given the structure IV, and the structure IVa must be regarded as less probable

However, the investigations of Nametkin, Isagulyants, Glagoleva, and Kholmer [4] on the course of the condensation of citral with 2-butanone have shown that the course of the reaction in an alkaline medium depends also on whether caustic alkali or sodium alkoxide is used as condensing agent. Condensation in presence of sodium ethoxide occurs in the 1-position, whereas in presence of caustic alkali it occurs in the 3-position of 2-butanone. The two methylionones obtained by "methyl-condensation" and "methylene-condensation" respectively differ inappreciably in physicochemical constants, whereas the melting points of their semicarbazones differ greatly.

By analogy with the results of Nametkin and Isagulyants it might be expected that the course of the condensation reaction of 3-camphenilanecarboxaldehyde with 2-butanone would depend on whether caustic alkali or sodium ethoxide is used. Investigations have shown, however, that our products were the same in both reactions. Their identity was confirmed not only by their physical constants, which in this case may not be sufficiently characteristic, but also by the identity of their semicarbazones: in both cases semicarbazones of m.p. 193-194° were obtained, and in admixture they showed no melting point depression. These results show that the course of the reaction is the same in both cases. We did not determine the structure of the ketone: as stated above, it appears most probable, on analogy with other investigations, that condensation occurs at the 1-position of 2-butanone (at the a-methyl)

Acetophenone and camphenilanecarboxaldehyde did not react in presence of aqueous alkali, and the condensation was performed in the presence of sodium ethoxide. The product, after distillation over camphorsulfonic acid, had the following constants: b.p. 175-176° (3 mm); n_D^{20} 1.5585; d_4^{20} 1.0365; Found MR 79.18; Calculated for $C_{19}H_{24}O$ F MR 76.87; exaltation 2.31. The yield of pure product was 42%.

The ketone obtained, 3-(3-camphenilyl)acrylophenone (V), was a viscous greenish-yellow liquid having a feeble spicy odor. Its semicarbazone melted at 167-169°.
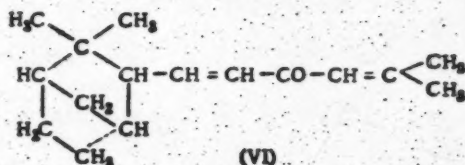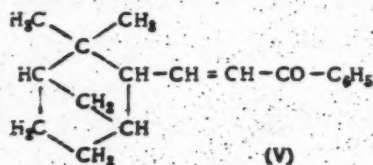
3-Camphenilanecarboxaldehyde readily condensed with mesityl oxide in presence of sodium ethoxide. The pure ketone, 1-(3-camphenilyl)-5-methyl-1,4-hexadien-3-one (VI), had the following constants: b.p. 131-133° (1.5 mm), n_D^{20} 1.5200; d_4^{20} 0.9627; Found MR 73.36; Calculated for $C_{16}H_{24}O$ F$_2$ MR 70.76; exaltation 2.60. The ketone was a thick oily liquid having a feeble spicy odor.

The condensation of 3-camphenilanecarboxaldehyde with 6-methyl-5-hepten-2-one went very readily in presence of sodium ethoxide. The ketone obtained, after distillation over camphorsulfonic acid, had the following constants: b.p. 166-167° (5 mm); n_D^{20} 1.5060; d_4^{20} 0.9496; Found MR 81.49; Calculated for $C_{18}H_{28}O$ F$_2$ MR 80.00; exaltation 1.49. No investigation to determine which of the two possible formulas (VII or VIIa) the ketone possessed

was   carried out. The ketone was a yellow oily liquid having a feeble spicy odor. The yield of pure product was 37%. The semicarbazone of the ketone melted at 152-153°.

(VII)   (VIIa)
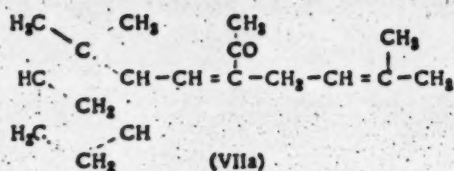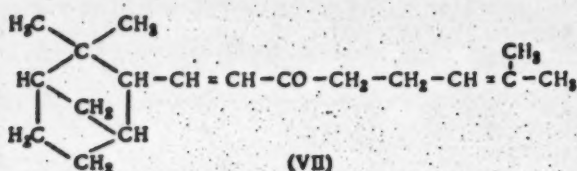
3-Camphenilanecarboxaldehyde condensed readily with ethyl acetate and with ethyl acetoacetate. The condensation product formed with ethyl acetate (VIII) had the following constants: b.p. 140-142° (10 mm); n_D^{20} 1.4890; d_4^{20} 0.9893; Found MR 64.85; Calculated for $C_{14}H_{22}O_2$ F MR 63.64; exaltation 1.21. The ester, which was obtained in 51.3% yield, was an oily liquid having a feeble odor.

The condensation of 3-camphenilanecarboxaldehyde with ethyl acetoacetate was carried out in presence of piperidine. The condensation product (IX) had the following constants: b.p. 137-138.5° (2.5 mm); n_D^{20} 1.4905; d_4^{20} 1.0238; Found MR 74.64; Calculated for $C_{16}H_{24}O_3$ F MR 72.89; exaltation 1.75. The ester IX was a liquid having a feeble pleasant odor. The yield of pure product was 46%.

(VIII)   (IX)
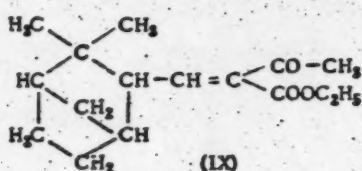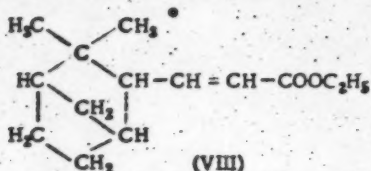
When the ethyl ester of α-acetyl-3-camphenilaneacrylic acid (IX) was treated with semicarbazide, a product of m.p. 157-159° was obtained, and this corresponded in its analysis not to the semicarbazone of the keto ester IX, but to the pyrazolone derivative X, which arose by the elimination of a molecule of alcohol from the semicarbazone:

(X)
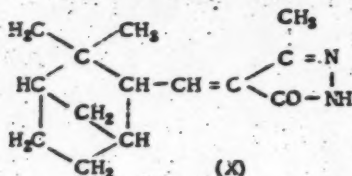
EXPERIMENTAL

The 3-camphenilanecarboxaldehyde that we used as starting material was obtained by the isomerization of camphene oxide in presence of zinc bromide. In its turn, camphene oxide was prepared by the oxidation of camphene by means of acetylene hydroperoxide in ether solution. The 3-campnenilanecarboxaldehyde boiled at 84° (12 mm) and melted at 65-67°.

Condensation of 3-Camphenilanecarboxaldehyde with Acetone.

To a mixture of 25 g of the aldehyde, 37 g of acetone, and 300 ml of water, 50 ml of 2 N caustic soda was added. The mixture was agitated in a shaker for 32 hours. The mixture was neutralized with tartaric acid and extracted with ether, and the ether extract was dried with calcined sodium sulfate. The ether was drawn off under slightly reduced pressure, and the residue was vacuum-fractionated from an Arbuzov flask. The following fractions were obtained:

Fraction I, b.p. 80-127° (12 mm); 10 g; n_D^{20} 1.4845

Fraction II, b.p. 127-139° (12 mm); 2.5 g; n_D^{20} 1.5000

Fraction III, b.p. 139-140° (12 mm); 13.5 g; n_D^{20} 1.5030; d_4^{20} 0.9705

Residue, 1 g of resin

Fraction III had a camphorlike odor.

Fractions II and III, after refractionation in presence of a crystal of camphorsulfonic acid, yielded a pure product of b.p 136-137° (11.5 mm); n_D^{20} 1.5008; d_4^{20} 0.9692; Found MR 58.69; Calculated for $C_{13}H_{20}O$ F MR 57.38; exaltation 1.31. The reaction product was a pale yellowish-green oily liquid having an odor reminiscent of that of ionone, but with a slight characteristic difference.

<div align="center">

Found %: C 80.83; 80.72; H 10.39; 10.30

$C_{13}H_{20}O$. Calculated %: C 81.17;   H 10.48

</div>

Preparation of the Semicarbazone. To a solution of 1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate in a small amount of water, 1.7 g of the condensation product of acetone with 3-camphenilanecarboxaldehyde was added, and pure methanol was added to this mixture until solution was complete. The solution was shaken and after 30 minutes the semicarbazone was precipitated, and was filtered off, washed with water, and dried (2.8 g of crude product). After three crystallizations, from ethanol and methanol alternately, the semicarbazone melted at 176-177°. After a fourth crystallization, the melting point did not change.

<div align="center">

Found %: N 16.92

$C_{14}H_{23}ON_3$ Calculated %: N 17.56

</div>

Condensation of 3-Camphenilanecarboxaldehyde with 2-Butanone

To a mixture of 20 g of the aldehyde, 36 g of 2-butanone, and 300 ml of water, 50 ml of 2 N caustic soda was added. The mixture was agitated in a shaker for 50 hours. The mixture was neutralized with tartaric acid and extracted with ether, and the ether extract was dried with sodium sulfate. The ether was drawn off, and the residue was vacuum-fractionated, yielding

Fraction I, b.p. 90-110° (17 mm), 3.4 g; n_D^{20} 1.4895

Fraction II, b.p. 110-150° (16 mm); 1.4 g; n_D^{20} 1.4890

Fraction III, b.p. 150-155° (16 mm); 10.7 g; n_D^{20} 1.4980

Residue 0.7 g

Fractions II and III were again vacuum-fractionated in presence of camphorsulfonic acid, when drops of water were noted in the condenser. A third fractionation yielded 8.2 g of condensation product having the following constants: b.p. 142-144° (12 mm); n_D^{20} 1.5000; d_4^{20} 0.9632; Found MR 62.99; Calculated for $C_{14}H_{22}O$ F MR 62.00; exaltation 0.99. The reaction product was an oily liquid, faintly greenish yellow in color, and having an odor reminiscent of that of ionone.

<div align="center">

Found %: C 81.17; H 10.77

$C_{14}H_{22}O$. Calculated %: C 81.52; H 10.75

</div>

The reaction was repeated under different conditions. A solution of 2 g of sodium in 40 ml of ethanol was added to a mixture of 18 g of the aldehyde and 10 g of 2-butanone. The temperature of the reaction mixture rose to 43°, and it became dark red in color. After three minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether. The ether extract was dried with sodium sulfate. Ether was drawn off, and the residue was vacuum-fractionated from an Arbuzov flask, yielding

Fraction I, b.p. 89-140° (11.5 mm); 4.5 g

Fraction II, b.p. 140-143.5° (11.5 mm); 3.7 g; n_D^{20} 1.4980

Fraction III, b.p. 143.5-148° (11.5 mm); 7.7 g; n_D^{20} 1.4990

Residue 3.8 g

Fractions II and III were distilled in presence of camphorsulfonic acid and yielded 9 g of the condensation product, which had the following constants: b.p. 140-142° (11.5 mm). n_D^{20} 1.5000; d_4^{20} 0.9630.

Preparation of the Semicarbazone. The substances taken for reaction were 1 g of semicarbazide hydrochloride, 1.5 g of sodium acetate, and 1.8 g of the condensation product of 2-butanone with 3-camphenilanecarboxaldehyde obtained in an aqueous solution of alkali. After 20 minutes the semicarbazone was precipitated (the weight of crude semicarbazone was 2.9g). After four recrystallizations from ethanol and methanol, the semicarbazone melted at 193-194°. A fifth recrystallization did not affect the melting point.

A semicarbazone was prepared also, in a similar way, from the condensation product prepared in presence of

sodium ethoxide. It melted at 193-194°, and when the two semicarbazones were mixed the melting point was not depressed.

Found %: N 15.97

$C_{16}H_{25}ON_3$. Calculated %: N 15.95

Condensation of 3-Camphenilanecarboxaldehyde with Acetophenone.

A mixture of 20 g of the aldehyde, 63 g of acetophenone, and 250 ml of water was taken and 40 ml of 2 N caustic soda was added. The reaction mixture was agitated on a shaker for 40 hours, and was then neutralized with tartaric acid and extracted with ether. The ether layer was dried with calcined sodium sulfate, and the ether was then drawn off, and the residue fractionated under reduced pressure. The whole of it came over at 85-87° (12 mm), which corresponds to the boiling point of the original aldehyde and acetophenone.

To the mixture of unchanged starting materials, a solution of 2 g of sodium in 40 ml of ethanol was added, when the temperature rose to 35°. After five minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether. The ether layer was dried with calcined sodium sulfate, and, after removal of the ether, the residue was vacuum-fractionated, yielding

Fraction I, b.p. 90-204° (12 mm): 4 g

Fraction II, b.p. 204-210° (12 mm): 17.7 g; n_D^{20} 1.5579.

A second fractionation yielded a product having b.p. 186-188° (6 mm); n_D^{20} 1.5580; d_4^{20} 1.035. This, after fractionation in presence of camphorsulfonic acid, gave a product having the following constants: b.p. 175-176° (3 mm); n_D^{20} 1.5585; d_4^{20} 1.0365; Found MR 79.18; Calculated for $C_{19}H_{24}O$ F_4 MR 76.87; exaltation 2.31. The reaction product was a thick oily liquid, greenish yellow in color, and having a faint spicy odor.

Found %: C 85.24; H 9.10

$C_{19}H_{24}O$. Calculated %: C 85.04; H 8.72

Preparation of the Semicarbazone. A mixture was prepared from 0.44 g of semicarbazide hydrochloride dissolved in methanol and 0.66 g of sodium acetate dissolved in a small amount of water; 1 g of the condensation product of 3-camphenilanecarboxaldehyde and acetophenone was added, and methanol was added until solution was complete. After five minutes a precipitate of the semicarbazone was obtained, and this was filtered off, washed with water, and dried (weight of crude semicarbazone, 0.7 g). After recrystallization from ethanol, from a mixture of benzene and ethanol, and then again from ethanol, the semicarbazone melted at 167-169°. A fourth recrystallization did not affect the melting point.

Found %: N 13.90

$C_{20}H_{27}ON_3$. Calculated %: N 13.49

Condensation of 3-Camphenilanecarboxaldehyde with Mesityl Oxide.

To a mixture of 20 g of the aldehyde and 15 g of mesityl oxide, a solution of 2 g of sodium in 40 ml of ethanol was added. The temperature rose to 40°. After three minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether; the ether layer was dried with sodium sulfate. The ether was drawn off, and the residue was vacuum-fractionated, yielding

Fraction I, b.p. to 110° (7 mm): 8 g

Fraction II, b.p. 110-152° (6 mm): 1.2 g; n_D^{20} 1.5150

Fraction III, b.p. 152-156° (5 mm): 15 g; n_D^{20} 1.5180

Residue, 7.2 g of a resinous mass

Fraction III was distilled in presence of camphorsulfonic acid, and then, as a result of a further fractionation, 13 g of a product having the following constants was obtained: b.p. 131-133° (1.5 mm); n_D^{20} 1.5200; d_4^{20} 0.9627; Found MR 73.36; Calculated for $C_{16}H_{24}O$ F_2 MR 70.76; exaltation 2.60. The condensation product was a yellow oily liquid having a feeble spicy odor.

Found %: C 82.30; H 10.51

$C_{16}H_{24}O$. Calculated %: C 82.70; H 10.41

Condensation of 3-Camphenilanecarboxaldehyde with 6-Methyl-5-hepten-2-one.

A solution of 1.5 g of sodium in 35 ml of ethanol was added to a mixture of 15.5 g of the aldehyde and 15 g of 6-methyl-5-hepten-2-one. The temperature rose to 45°, and after three minutes the solution was neutralized with

tartaric acid, diluted with water, and extracted with ether. The ether extract was dried with sodium sulfate, and, after removal of ether, the residue was vacuum-fractionated, yielding

Fraction I, b.p. to 176° (12 mm); 8 g

Fraction II, b.p. 176-187° (11.5 mm); 3 g; n_D^{20} 1.5043

Fraction III, b.p. 187-189.5° (11.5 mm); 12.3 g n_D^{20} 1.5050

Residue: 4.1 g of resin

Fractions II and III were distilled over camphorsulfonic acid, and refractionation of these fractions then yielded 9.8 g of a product having the following constants: b.p. 166-167° (5 mm); n_D^{20} 1.5060; d_4^{20} 0.9496; Found MR 81.49; Calculated for $C_{18}H_{28}O$ F$_2$ MR 80.0; exaltation, 1.49. The condensation product was a yellow oily liquid having a spicy odor.

Found %: C 83.37; 83.16; H 11.21; 10.98
$C_{18}H_{28}O$. Calculated %: C 83.01; H 10.84

Preparation of the Semicarbazone. The substances taken for reaction were 0.77 g of semicarbazide hydrochloride, 1.15 g of sodium acetate, and 1.8 g of the condensation product of 3-camphenilanecarboxaldehyde with 6-methyl-5-hepten-2-one. A precipitate appeared after one hour (weight of crude semicarbazide, 2.1 g). After three recrystallizations from benzene and ethanol, the semicarbazone melted at 152-153°. A fourth recrystallization did not affect the melting point.

Found %: N 13.32
$C_{19}H_{31}ON_3$ Calculated %: N 13.23

Condensation of 3-Camphenilanecarboxaldehyde with Ethyl Acetate.

Sodium (6 g) was granulated under a layer of dry toluene, the toluene was poured off, and a mixture, cooled to 0°, of 100 ml of ethyl acetate and 1 ml of absolute alcohol was poured over the sodium. The mixture was cooled with snow and energetically stirred for one hour while a solution of 20 g of 3-camphenilanecarboxaldehyde in 20 ml of ethyl acetate was added dropwise. When the whole of the aldehyde had been added, the reaction mixture was stirred vigorously until the whole of the sodium had reacted. An addition was then made of 18 ml of glacial acetic acid, and the mixture was cautiously diluted with water. The ethyl acetate layer was separated, and the water layer was extracted with ethyl acetate. The united extracts were washed with 120 ml of 6 N hydrochloric acid, and were then washed several times with water and dried with sodium sulfate. The solvent was removed in a water bath, and the residue was vacuum-fractionated, yielding

Fraction I, b.p. to 125° (11 mm); 1 g

Fraction II, b.p. 125-140° (11 mm); 3 g; n_D^{20} 1.4880

Fraction III, b.p. 140-143° (11 mm); 16.9 g; n_D^{20} 1.4885

Residue: 4.7 g of resin

A second fractionation of Fraction III yielded 15 g of the condensation product, which had the following constants: b.p. 140-142° (10 mm); n_D^{20} 1.4890; d_4^{20} 0.9893; Found MR 64.85; Calculated for $C_{14}H_{22}O_2$ F MR 63.64; exaltation 1.21. It was a greenish-yellow liquid having a faint, pleasant odor.

Found %: C 75.81; H 9.82
$C_{14}H_{22}O_2$ Calculated %: C 75.62; H 9.98

Condensation of 3-Camphenilanecarboxaldehyde with Ethyl Acetoacetate.

A mixture of 20 g of the aldehyde and 17 g of ethyl acetoacetate was cooled to -10-15°, and 1.5 g of piperidine was added. The mixture was set aside in the cold. After 48 hours the reaction mixture was neutralized with dilute sulfuric acid, washed with water, and extracted with ether. The ether layer was dried with sodium sulfate, and the ether was drawn off under reduced pressure. The residue was vacuum-fractionated, and yielded

Fraction I, b.p. to 115° (12.5 mm); 4 g

Fraction II, b.p. 115-168° (12.5 mm); 2.5 g; n_D^{20} 1.4807

Fraction III, b.p. 168-172° (12.5 mm); 17 g; n_D^{20} 1.4882

Residue, 3.3 g

Two fractionations of Fraction III yielded a product (15.9 g) having the following constants: b.p. 137-138.5' (2.5 mm); n_D^{20} 1.4905; d_4^{20} 1.0238; Found MR 74.64; Calculated for $C_{16}H_{26}O_3$ MR 72.89; exaltation 1.75. Σ was a colorless liquid of pleasant odor.

$$\text{Found \%:} \quad C\ 72.71;\ H\ 9.06$$
$$C_{16}H_{26}O_4 \quad \text{Calculated \%:} \quad C\ 72.69;\ H\ 9.15$$

Preparation of the Semicarbazone. The substances taken for reaction were 0.63 g of semicarbazide hydrochloride, 0.90 g of sodium acetate, and 1.5 g of the condensation product of 3-camphenilanecarboxaldehyde with ethyl acetoacetate. After two hours a precipitate appeared (1 g). Its melting point after two recrystallizations from alcohol was 157-159°.

$$\text{Found \%:} \quad N\ 12.32$$
$$C_{17}H_{27}O_3N_3 \quad \text{Calculated \%:} \quad N\ 13.07$$
$$C_{16}H_{25}ON_3 \quad \text{Calculated \%:} \quad N\ 12.06$$

SUMMARY

1. 3-Camphenilanecarboxaldehyde has been condensed with acetone, with 2-butanone, with acetophenone, with mesityl oxide, and with 6-methyl-5-hepten-2-one. The products formed from acetone and 2-butanone have odors that are reminiscent of that of ionone, and the products obtained from the other ketones have pleasant feeble spicy odors.

2. 3-Camphenilanecarboxaldehyde has been condensed with ethyl acetate and with ethyl acetoacetate, yielding the corresponding unsaturated esters.

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REACTIONS OF BIS(CHLOROMETHYL) ETHERS OF GLYCOLS

WITH SODIUM ALKOXIDES

B. A. Arbuzov and G. M. Vinokurova

Alkyl halomethyl ethers have been known for a long time. Bis(chloromethyl) ether was prepared in the middle of the last century by the chlorination of methanol [1]. In subsequent years some of the alkyl halomethyl ethers attracted the attention of Butlerov [2]. More detailed investigations of halomethyl ethers were made by Tishchenko [3], Henry [4], and Litterscheld and Thimme [5]. The main method used for the preparation of alkyl chloromethyl ethers was by the action of an alcohol and hydrochloric acid on formaldehyde [4].

In 1945 the chloromethylation reaction was used for the preparation of the chloromethyl ethers of various glycols [6, 7]. In the case of glycols the chloromethylation reaction is more complex and is accompanied by the formation of cyclic formals:

$$(CH_2)_n \underset{OH}{\overset{OH}{<}} + CH_2O = (CH_2)_n \underset{O}{\overset{O}{<}} CH_2 + H_2O.$$
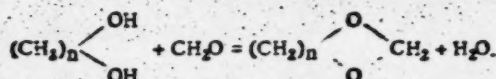
The object of the present work was the preparation of new glycol ethers, which have begun to acquire also some practical interest. We have prepared bis(chloromethyl) ethers of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 2-butyne-1,4-diol and have studied their reactions with sodium methoxide, ethoxide, isopropoxide, butoxide, and isobutoxide; the 1,2- and 1,3-propanediol ethers were prepared for the first time. The constants of the chloromethyl ethers obtained are given in Table 1.

TABLE 1

Bis(chloromethyl) ether of	B.p. in °C (pressure in mm Hg)	d_4^{20}	n_D^{20}	Yield (%)
Ethylene glycol	102-105 (23)	–	–	80
1,2-Propanediol	87-88 (12)	1.2206	1.4575	44.3
1,3-Propanediol	99-103 (14)	1.2254	1.4600	79.1
1,3-Butanediol	106.5-110 (13)	1.1824	1.4572	21.0
2-Butyne-1,4-diol	150-152 (14)	–	1.4920	55.6

In the chloromethylation of ethyleneglycol, 1,3-propanediol, and 2-butyne-1,4-diol, we obtained only bis(chloromethyl) ethers. In the case of 1,3-butanediol, we obtained also a cyclic formal.

As the work of Lichtenberger and Martin [6] and of Dupont [7] has shown, when sodium ethoxide reacts with chloromethyl ethers of glycols, bis(ethoxymethyl) ethers of glycols are obtained. We have now carried out the reactions of bis(chloromethyl) ethers of glycols with sodium alkoxides in a medium of the corresponding alcohol; the reactions of the bis(chloromethyl) ether of ethylene glycol with sodium butoxide and with sodium isobutoxide were carried out also in an ether medium, in absence of the alcohol. In the case of the bis(chloromethyl) ethers of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 2-butyne-1,4-diol treated with sodium methoxide or ethoxide, the reaction proceeded normally, and the corresponding methoxymethyl and ethoxymethyl ethers were obtained in 43-88% yields. The constants of the ethers obtained are given in Table 2.

When the bis(chloromethyl) ethers of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 2-butyne-1,4-diol were treated with sodium alkoxides derived from isopropyl and higher alcohols, certain departures from the normal reaction were observed. In most cases, in addition to the normal reaction products, a formal was isolated. In the reactions between the bis(chloromethyl) ether of ethylene glycol and sodium isobutoxide and between the bis(chloromethyl) ether of 1,2-propanediol and sodium butoxide, in addition to the corresponding formals and full ethers of the glycols, products were isolated that corresponded in physicochemical constants and elementary

TABLE 2

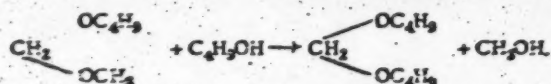| Bis(alkoxymethyl) ethers of glycols	B. p in °C (pressure in mm Hg)	n_D^{20}	d_4^{20}	MR Found	MR Calculated	Yield (%)
$CH_3OCH_2OCH_2CH_2OCH_2OCH_3$ CH_3	65-67 (15)	1.4033	1.0027	36.52	36.48	56.61
$CH_3OCH_2OCH_2CHOCH_2OCH_3$ CH_3	68-70 (14)	1.4045	0.9814	40.92	41.09	43.63
$C_2H_5OCH_2OCH_2CHOCH_2OC_2H_5$	87-89 (14)	1.4103	0.9403	50.60	50.33	57.20
$CH_3OCH_2OCH_2CH_2CH_2OCH_2OCH_3$	62-63.5 (8)	1.4100	0.9946	40.85	40.09	42.95
$C_2H_5OCH_2OCH_2CH_2CH_2OCH_2OC_2H_5$	97.5-99 (15)	1.4130	0.9470	50.55	50.33	88.33
$CH_3OCH_2OCH-CH_2CH_2OCH_2OCH_2$ CH_3	78-80 (12)	1.4120	0.9760	45.39	45.71	64.90
$C_2H_5OCH_2OCHCH_2CH_2OCH_2OC_2H_5$ CH_3	101-102 (14)	1.4148	0.9387	54.93	54.95	72.73
$CH_3OCH_2OCH_2C\equiv CCH_2OCH_2OCH_3$	114-116 (13.5)	1.4417	1.0493	43.85	43.71	89.43

analysis to mono(alkoxymethyl) ethers of glycols. The reactions of the bis(chloromethyl) ether of ethylene glycol with sodium isopropoxide and with sodium butoxide, however, proceeded in quite a different way from the others. In the first reaction it was not found possible to isolate any of the bis(isopropoxymethyl) ether, the products obtained being the formal (diisopropoxymethane), the mono(isopropoxymethyl) ether of ethylene glycol, and a mixture of high-boiling substances which could not be separated by distillation. In the reaction with sodium butoxide, in addition to the formal and the normal reaction product, a high-boiling substance was isolated which corresponded in physicochemical constants and analysis to the substance of formula

$$C_4H_9OCH_2OCH_2CH_2OCH_2CH_2OCH_2OC_4H_9$$
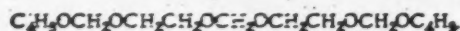
We may suggest, in explanation of the formation of all these anomalous products, that they result from the partial alcoholysis of the normal reaction products, i.e. bis(alkoxymethyl) ethers of glycols. The suggestion of the possibility of the partial alcoholysis of bis(alkoxymethyl) ethers of glycols is confirmed by some investigations of Mamedov carried out in 1942. Mamedov [8] found that dialkoxymethanes undergo alcoholysis, even in an alkaline medium, an alkoxy group of the ether being replaced by the alkoxy group of the alcohol used:

$$CH_2 \begin{matrix} OC_4H_9 \\ OCH_3 \end{matrix} + C_4H_9OH \longrightarrow CH_2 \begin{matrix} OC_4H_9 \\ OC_4H_9 \end{matrix} + CH_3OH$$

However, experiments that we have carried out on the alcoholysis of the bis(butoxymethyl) ether of ethylene glycol, the bis(ethoxymethyl) ether of 1,3-propanediol, and the bis(isobutoxymethyl) ether of 1,3-butanediol in weakly alkaline medium did not give positive results. Guben [9] has also remarked on the high stability of acetals toward alkaline reagents. In weakly acid medium the alcoholysis of glycol ethers goes much more readily and in quantitative yield; this was noted both by Mamedov and by us.

The alcoholysis of bis(alkoxymethyl) ethers of glycols may be represented by the following scheme:

$$(CH_2)_x \begin{matrix} CH_2OCH_2Cl \\ \\ CH_2OCH_2Cl \end{matrix} + 2RONa \longrightarrow (CH_2)_x \begin{matrix} CH_2OCH_2OR \\ \\ CH_2OCH_2OR \end{matrix} + 2NaCl; \quad (1)$$

$$(CH_2)_x \begin{matrix} CH_2OCH_2OR \\ \\ CH_2OCH_2OR \end{matrix} + ROH \longrightarrow CH_2 \begin{matrix} OR \\ \\ OR \end{matrix} + (CH_2)_x \begin{matrix} CH_2OH \\ \\ CH_2OCH_2OR \end{matrix} \quad (2)$$

$$(CH_2)_x \begin{matrix} CH_2OH \\ \\ CH_2OCH_2OR \end{matrix} + (CH_2)_x \begin{matrix} CH_2OCH_2OR \\ \\ CH_2OCH_2OR \end{matrix} \longrightarrow ROH + CH_2 \begin{matrix} O-CH_2(CH_2)_x CH_2OCH_2OR \\ \\ O-CH_2(CH_2)_x CH_2OCH_2OR \end{matrix} \quad (3)$$
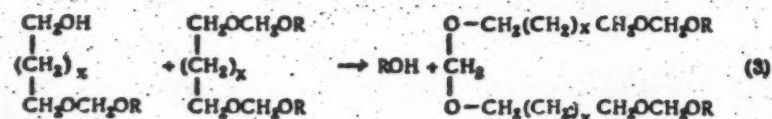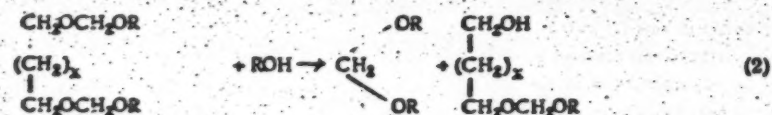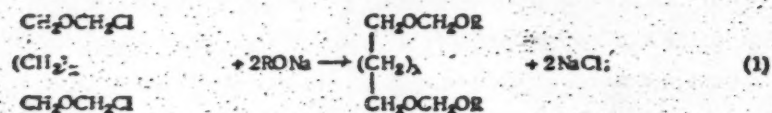
TABLE 3

Reaction Product	B.p. in °C (pressure in mm Hg)		n_D^{20}	d_4^{20}	MR Found	MR Calculated
(i-C₃H₇O)₂CH₂	117-120		1.3895	0.8206	38.09	37.81
i-C₃H₇OCH₂OCH₂CH₂O H . . .	79-80	(14)	1.4192	0.9771	35.18	34.72
n-C₄H₉O)₂CH₂	66-67	(13)	1.4068	0.8397	46.88	47.05
n-C₄H₉OCH₂OCH₂CH₂ . . . . O	132-134	(13)	1.4210	0.9247	64.16	64.18
i-C₄H₉OCH₂ C₄H₉OCH₂OCH₂CH₂O CH₂ . . .	183-186	(13)	1.4302	0.9797	81.22	81.32
C₄H₉OCH₂OCH₂CH₂O (i-C₄H₉O)CH₂	64	(25)	1.4005	0.8254	47.03	47.05
i-C₄H₉OCH₂OCH₂CH₂OH . . .	89-90.5	(15)	1.4200	0.9492	39.34	39.46
i-C₄H₉OCH₂OCH₂	124-125	(15)	1.4173	0.9185	64.47	64.18
i-C₄H₉OCH₂OCH₂ i-C₃H₇OCH₂OCH₂	101-102	(12)	1.4130	0.9170	59.82	59.57
i-C₃H₇OCH₂OCH−CH₃ C₄H₉OCH₂OCH₂CHOH . . . . . CH₃	85-86	(9)	1.4250	0.9401	44.08	43.95
C₄H₉OCH₂OCH₂CHOCH₂OC₄H₉ CH₃	142-143	(15)	1.4240	0.9131	69.27	68.80
i-C₄H₉OCH₂OCH₂ . . . . i-C₄H₉OCH₂OCH−CH₃	129-131	(14)	1.4190	0.9062	68.97	68.80
i-C₃H₇OCH₂OCH₂ CH₂ . . . . i-C₃H₇OCH₂OCH₂	106-109	(13)	1.4160	0.9220	59.87	59.57
C₄H₉OCH₂OCH₂ CH₂ . . . . . C₄H₉OCH₂OCH₂	136-138	(9)	1.4255	0.9199	69.00	68.81
i-C₄H₉OCH₂OCH₂ CH₂ . . . . i-C₄H₉OCH₂OCH₂	120-123	(8)	1.4225	0.9117	69.19	68.81
CH₃ i-C₃H₇OCH₂OCH CH₂ . . . . . i-C₃H₇OCH₂OCH₂	113-116	(11)	1.4170	0.9159	64.25	64.18
CH₃ C₄H₉OCH₂OCH CH₂ . . . . . . C₄H₉OCH₂OCH₂	152-154	(15)	1.4260	0.9163	73.26	73.42
CH₃ i-C₄H₉OCH₂OCH CH₂ . . . . . i-C₄H₉OCH₂OCH₂	130-131.5	(8.5)	1.4235	0.9064	73.68	73.42
i-C₃H₇OCH₂OCH₂C . . . . . i-C₃H₇OCH₂OCH₂C	138-140	(13.5)	1.4398	0.9748	62.16	62.18
C₄H₉OCH₂OCH₂C . . . . C₄H₉OCH₂OCH₂C	155-158	(6)	1.4437	0.9574	71.53	71.39
i-C₄H₉OCH₂OCH₂C . . . . . i-C₄H₉OCH₂OCH₂C	145	(6)	1.4400	0.9506	71.53	71.39

In this way the formation of all the by-products can be explained. The constants of the ethers obtained are shown in Table 3:

It should be noted that all of the substances given in the table, with the exception of diisopropoxy-, dibutoxy- and diisobutoxy-methanes and the bis(butoxymethyl) ether of ethylene glycol, were prepared for the first time, the constants of the compounds that have been prepared previously were completely in accord with the values obtained by Mamedov.

However, a number of our results do not agree with those of Mamedov. In carrying out the synthesis of the mono(isobutoxymethyl) ester of ethylene glycol according to the equation

$$CH_2OH \atop CH_2OH \quad + ClCH_2OCH_2C_4H_9-i + NaOH \rightarrow \quad {CH_2OCH_2OC_4H_9-i \atop | \atop CH_2OH} + H_2O + NaCl$$
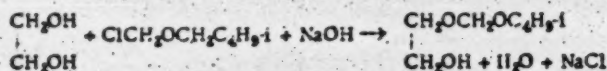
Mamedov obtained two fractions. He considered the first fraction b.p. 80-88° [11 mm]; $d_{4\circ}^{20}$ 0.8399; n_D^{20} 1.4047 to

be the product of the dehydration of the hydroxy ether $CH_2 {OC_4H_9-i \atop OCH = CH_2}$, and in support of his contention Mamedov

cited molecular-weight determinations (cryoscopical in benzene), double-bond estimation, and elementary analysis:

Found %: Br_2 0.2308; C 63.77; H 11.47; M 138.3
Calculated %: Br_2 0.2123; C 64.71; H 10.77; M 130

He regarded the second fraction b.p. 110-118° [5 mm]; d_{20}^{20} 0.9188; n_D^{20} 1.4165 as the mono(isobutoxymethyl) ether of ethylene glycol: Found M 150.37; MR 40.59; Calculated M 148; MR 39.33;

Found %: OH 12.3; C 56.75; H 11.59
Calculated %: OH 11.48; C 57.00; H 10.8

In the reaction between the bis(chloromethyl) ether of ethylene glycol and sodium isobutoxide we also obtained two products, their constants being:

1. B.p. 89-90.5° (15 mm); n_D^{20} 1.4200; d_4^{20} 0.9492; Found MR 39.34; Calculated for $C_7H_{16}O_3$ MR 39.46

Found %: C 56.40; H 10.47
Calculated %: C 56.75; H 10.81

2. B.p. 124-125° (15 mm); n_D^{20} 1.4173; d_4^{20} 0.9185; Found MR 64.47; Calculated for $C_{12}H_{26}O_4$ MR 64.18

Found %: C 61.29; H 11.32
Calculated %: C 61.53; H 11.11

By reference to the molecular refraction and elementary analysis we established that the product of b.p. 89-90.5° (15 mm) was the mono(isobutoxymethyl) ether of ethylene glycol, and the product of b.p. 124-125° (15 mm) was the bis(isobutoxymethyl) ether of ethylene glycol. Thus a comparison of our results with those of Mamedov shows that products having similar physical constants have been taken to be two different compounds, and the constants of our mono(isobutoxymethyl) ether of ethylene glycol and Mamedov's mono(isobutoxymethyl) ether of ethylene glycol do not correspond with each other.

A study of our results and those of Mamedov concerning the products of b.p. 110-118° (5 mm) and 124-125° (15 mm) forces one to the conclusion that we are dealing here with one and the same bis(isobutoxymethyl) ether of ethylene glycol, the only difference being that Mamedov's product was impure. In fact, the wide boiling range (8°) of Mamedov's product, and consequently the large discrepancy between theoretical and practical values of the molecular refraction, and also the analytical data —all these confirm this suggestion. The only perplexing point is Mamedov's analysis for hydroxyl. The cause of the difference in the experimental results obtained in our work and in that of Mamedov can be determined only by a verification of Mamedov's results [10].

EXPERIMENTAL

Preparation of the Bis(chloromethyl) Ether of 1,2-Propanediol

The bis(chloromethyl) ether of 1,2-propanediol was prepared by the chloromethylation of 1,2-propanediol by the method developed by Lichtenberger and Martin, and also by Dupont and coworkers [6, 7]. A mixture of 200 g of 1,2-propanediol and 155.8 g of powdered paraformaldehyde was introduced into a round-bottomed flask

surrounded with a cooling mixture, and was stirred carefully. A stream of dry hydrogen chloride was passed through the mixture until full saturation was attained. After 5-6 hours, two layers formed. The upper, water layer was poured off, and the lower layer was dried with calcium chloride and fractionated from an Arbuzov flask. The fractionation yielded the bis(chloromethyl) ether of 1,2-propanediol, yield 44-45%; b.p. 87-68° (12 mm); d_4^{20} 1.2195; n_D^{20} 1.4592; Found MR 39.03; Calculated for $C_5H_{10}O_2Cl_2$ MR 39.41.

<div align="center">

Found %: Cl 41.20

$C_5H_{10}O_2Cl_2$ Calculated %: Cl 41.04

</div>

The bis(chloromethyl) ether of 1,2-propanediol is a clear liquid that fumes in air and has a sharp odor and lachrymatory properties.

Preparation of the Bis(chloromethyl) Ether of 1,3-Propanediol

The bis(chloromethyl) ether of 1,3-propanediol was prepared similarly to all of the other such glycol ethers. A current of dry hydrogen chloride was passed through a mixture of 145.5 g of 1,3-propanediol and 114.5 g of paraformaldehyde. When saturation was complete, the two layers formed were separated. The lower layer, an oily liquid, was dried with calcium chloride and fractionated from an Arbuzov flask. Two fractionations yielded the required ether in 79.10% yield; it had b.p. 99-103: (12 mm); d_4^{20} 1.2254; n_D^{20} 1.4600; Found MR 38.67; Calculated for $C_5H_{10}O_2Cl_2$ MR 38.31

<div align="center">

Found %: Cl 41.24

$C_5H_{10}O_2Cl_2$ Calculated %: Cl 41.04

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The bis(chloromethyl) ether of 1,3-propanediol is a heavy liquid that fumes lightly in air and has a sharp odor and somewhat lachrymatory properties.

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of Ethylene Glycol

A solution of sodium methoxide was prepared in a 500-ml round-bottomed flask, fitted with reflux condenser and dropping funnel, by addition of 11.5 g of sodium to 200 ml of absolute methanol, and was cooled to about room temperature. To the constantly stirred solution, 50 g of the bis(chloromethyl) ether of ethylene glycol was then added dropwise, when a precipitate of sodium chloride immediately appeared and the reaction mixture became warm. Reaction was completed by heating of the mixture in a water bath for one hour. The sodium chloride was filtered off, and the filtrate was fractionated from a flask provided with a Widmer column. The fractionation gave a 56.61% yield of the bis(methoxymethyl) ether of ethylene glycol, b.p. 65-67° (15 mm); d_4^{22} 1.0027; n_D^{20} 1.4033; Found MR 36.52; Calculated for $C_6H_{14}O_4$ MR 36.48

<div align="center">

Found %: C 47.96; H 9.10

$C_6H_{14}O_4$ Calculated %: C 48.00; H 9.33

</div>

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of Ethylene Glycol

The bis(chloromethyl) ether of ethylene glycol (30 g) was added dropwise with shaking of the flask to a solution of sodium isopropoxide prepared from 8.6 g of sodium and 300 ml of absolute isopropyl alcohol. The procedure was similar to that of the preceding experiment, heating in the water bath being for one hour. Repeated fractionation yielded:

1. Diisopropoxymethane in 24.49% yield, b.p. 117-120°; d_4^{20} 0.8206; n_D^{20} 1.3895; Found MR 37.09; Calculated for $C_7H_{16}O_2$ MR 37.81. Mamedov found b.p. 118-119°; n_D^{20} 1.3865; d_4^{20} 0.8197.

2. The mono(isopropoxymethyl) ether of ethylene glycol, b.p. 79-80° (14 mm); d_4^{20} 0.9771; n_D^{20} 1.4194; Found MR 35.18; Calculated for $C_6H_{14}O_3$ MR 34.72.

<div align="center">

Found %: C 53.38; H 10.40

$C_6H_{14}O_3$ Calculated %: C 53.73; H 10.44

</div>

3. A mixture of high-boiling products, which it was not found possible to fractionate.

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of Ethylene Glycol

Experiment 1. The bis(chloromethyl) ether of ethylene glycol (30 g) was added dropwise to a constantly shaken solution of sodium butoxide prepared from 8.6 g of sodium and 220 ml of absolute butyl alcohol. The mixture was heated in an oil bath for 90 minutes. Fractionation yielded dibutoxymethane in 87.70% yield; it had b.p. 66-67° (13 mm); d_4^{20} 0.8397; n_D^{20} 1.4067; Found MR 46.30; Calculated for $C_9H_{20}O_2$ MR 47.05

<div align="center">

Found %: C 67.19; H 12.49

$C_9H_{20}O_2$ Calculated %: C 67.5; H 12.5

</div>

Experiment 2. The reaction between sodium butoxide and the bis(chloromethyl) ether of ethylene glycol was repeated under somewhat different conditions. The alkoxide was prepared by the swelling method [11], and the reaction was carried out in an ether medium, as follows. The bis(chloromethyl) ether of ethylene glycol (45 g) was added dropwise to 53 g of sodium butoxide in absolute ether, when the reaction flask became somewhat warm. When addition of the chloro ether was complete, the reaction was continued by heating the mixture in a water bath for ten hours. Even after this prolonged heating, however, reaction was not complete. In order to free the mixture from the bis(chloromethyl) ether of ethylene glycol, which would have inevitably interfered in the fractionation, the contents of the flask were treated with water, the reaction product was extracted with ether, and the ether extract was dried with calcium chloride and then fractionated, yielding:

1. Dibutoxymethane in 34.72% yield: it had b.p. 65-69.5° (15 mm); d_4^{20} 0.8378; n_D^{20} 1.4090; Found MR 47.24; Calculated for $C_9H_{20}O_2$ MR 47.05.

2. The bis(butoxymethyl) ether of ethylene glycol, b.p. 132-134° (13 mm); d_4^{20} 0.9247; n_D^{20} 1.4210; Found MR 64.16; Calculated for $C_{12}H_{26}O_4$ MR 64.18; yield 17.22%;

$$C_{12}H_{26}O_4 \qquad \text{Found \%: } C\ 61.29;\ H\ 11.02 \qquad \text{Calculated \%: } C\ 61.53;\ H\ 11.11$$

3. $C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9$ in 5.86% yield; it had the following constants: b.p. 153-156° (13 mm); d_4^{20} 0.9797, n_D^{20} 1.4302; Found MR 81.22; Calculated for $C_{15}H_{32}O_6$ MR 81.32.

$$C_{15}H_{32}O_6 \qquad \text{Found \%: } C\ 58.37;\ H\ 10.22 \qquad \text{Calculated \%: } C\ 58.44;\ H\ 10.38$$

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of Ethylene Glycol

Experiment 1. The reaction was carried out in the usual way. The bis(chloromethyl) ether of ethylene glycol (50 g) was added to a solution of sodium isobutoxide prepared from 14.4 g of sodium and 200 ml of absolute isobutyl alcohol, and the reaction was completed by heating the mixture in an oil bath for three hours. Fractionation of the reaction products yielded:

1. Diisobutoxymethane in 70.15% yield; it had b.p. 63-64° (25 mm); d_4^{20} 0.8254; n_D^{20} 1.4005; Found MR 47.03; Calculated for $C_9H_{20}O_2$ MR 47.05.

$$C_9H_{20}O_2 \qquad \text{Found \%: } C\ 66.99;\ H\ 12.15 \qquad \text{Calculated \%: } C\ 67.5;\ H\ 12.5$$

The literature gives b.p. 164.3° and n_D^{20} 1.4020 [12]

2. The mono(isobutoxymethyl) ether of ethylene glycol (7.7 g), b.p. 89-90.5° (15 mm); d_4^{20} 0.9492; n_D^{20} 1.4200; Found MR 39.34; Calculated for $C_7H_{16}O_3$ MR 39.46.

$$C_7H_{16}O_3 \qquad \text{Found \%: } C\ 56.40;\ H\ 10.47 \qquad \text{Calculated \%: } C\ 56.75;\ H\ 10.81$$

3. The bis(isobutoxymethyl) ether of ethylene glycol (7.2 g), b.p. 124-125° (15 mm); d_4^{20} 0.9185; n_D^{20} 1.4173; Found MR 64.47; Calculated for $C_{12}H_{26}O_4$ MR 64.18.

$$C_{12}H_{26}O_4 \qquad \text{Found \%: } C\ 61.29;\ H\ 11.32 \qquad \text{Calculated \%: } C\ 61.53;\ H\ 11.11$$

Experiment 2. The reaction between sodium isobutoxide and the bis(chloromethyl) ether of ethylene glycol was repeated under different conditions. The alkoxide was prepared by the swelling method. To 53 g of sodium isobutoxide in ether, 50 g of the bis(chloromethyl) ether of ethylene glycol was added dropwise, and when the whole of the chloro ether had been added, the reaction flask was heated in a water bath for ten hours. However, in this case also reaction did not go to completion. In order, therefore, to hydrolyze unchanged chloro ether, the contents of the flask were treated with water, and the reaction products were extracted with ether. The ether extract was dried with calcium chloride, the ether was driven off, and the residue was fractionally distilled from a flask having a Widmer column. The products were: 19.8 g of diisobutoxymethane, b.p. 59-64° at 21 mm; n_D^{20} 1.4010 (the literature gives b.p. 164.3°; n_D^{20} 1.4020 [12]) and 8 g of the bis(isobutoxymethyl) ether of ethylene glycol, b.p. 119-121° (12 mm); d_4^{20} 0.9160; n_D^{20} 1.4179; Found MR 64.37; Calculated for $C_{12}H_{26}O_4$ MR 64.18. It was not found possible to isolate any pure substance by fractionation of the high-boiling fraction.

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The substances taken for reaction were 10.2 g of sodium, 200 ml of absolute methanol, and 30 g of the bis(chloromethyl) ether of 1,2-propanediol. The mixture was heated in the water bath for one hour. The

bis(methoxymethyl) ether of 1,2-propanediol was isolated in 43.63% yield; it had b.p. 68-70° (14 mm); d_4^{20} 0.9814; n_D^{20} 1 4045; Found MR 40.92; Calculated for $C_7H_{16}O_4$ MR 41.09.

$$\text{Found \%:} \quad C\ 51.31;\ H\ 9.94$$
$$C_7H_{16}O_4 \quad \text{Calculated \%:} \quad C\ 51.22;\ H\ 9.75$$

Action of Sodium Ethoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The bis(chloromethyl) ether of 1,2-propanediol (20 g) was added dropwise to a solution of 15.7 g of sodium ethoxide in 250 ml of absolute alcohol, and the mixture was heated in a water bath for one hour. The bis(ethoxymethyl) ether of 1,2-propanediol was isolated in 57.20% yield; it had b.p. 87-89° (14 mm); d_4^{20} 0.9408; n_D^{20} 1.4103; Found MR 50.60; Calculated for $C_9H_{20}O_4$ MR 50.33.

$$\text{Found \%:} \quad C\ 56.10;\ H\ 10.52$$
$$C_9H_{20}O_4 \quad \text{Calculated \%:} \quad C\ 56.25;\ H\ 10.41$$

The ether so obtained is a clear liquid having a pleasant feeble odor.

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The substances taken for reaction were 15 g of the bis(chloromethyl) ether of 1,2-propanediol and 14.2 g of sodium isopropoxide. The mixture was heated in a water bath for one hour. The bis(isopropoxymethyl) ether of 1,2-propanediol was isolated in 54.73% yield; it had b.p. 101-102° (12 mm); d_4^{20} 0.9170; n_D^{20} 1.4130; Found MR 59.82; Calculated for $C_{11}H_{24}O_4$ MR 59.57.

$$\text{Found \%:} \quad C\ 59.63;\ H\ 10.83$$
$$C_{11}H_{24}O_4 \quad \text{Calculated \%:} \quad C\ 60.00;\ H\ 10.90$$

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The substances taken for reaction were 30 g of the bis(chloromethyl) ether of 1,2-propanediol and 33.3 g of sodium butoxide. The mixture was heated in an oil bath for one hour. As a result of the reaction, three substances were obtained:

1. Dibutoxymethane (10.3 g), b.p. 47-48° at 4 mm; d_4^{20} 0.8378; n_D^{20} 1.4090; Found MR 47.24; Calculated for $C_9H_{20}O_2$ MR 47.05.

2. The mono(butoxymethyl) ether of 1,2-propanediol, b.p. 85-86° (9 mm); d_4^{20} 0.9401; n_D^{20} 1.4250; Found MR 44.03; Calculated for $C_8H_{18}O_3$ MR 43.95. (7 g).

$$\text{Found \%:} \quad C\ 59.33;\ H\ 11.23$$
$$C_8H_{18}O_3 \quad \text{Calculated \%:} \quad C\ 59.25;\ H\ 11.11$$

3. The bis(butoxymethyl) ether of 1,2-propanediol, (14 g), b.p. 142-143° (15 mm); d_4^{20} 0.9131; n_D^{20} 1.4240; Found MR 69.27; Calculated for $C_{13}H_{28}O_4$ MR 68.80.

$$\text{Found \%:} \quad C\ 62.68;\ H\ 11.24$$
$$C_{13}H_{28}O_4 \quad \text{Calculated \%:} \quad C\ 62.9;\ H\ 11.29$$

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of 1,2-Propanediol

The procedure was similar to that of the reactions described above. The reactants were 20 g of the bis(chloromethyl) ether of 1,2-propanediol and 22.19 g of sodium isobutoxide, and the mixture was heated in an oil bath for one hour. The products isolated were 9 g of diisobutoxymethane, b.p. 48-52° at 13 mm; n_D^{20} 1.4020; and 12.2 g of the bis(isobutoxymethyl) ether of 1,2-propanediol, b.p. 127-128° at 14 mm; d_4^{20} 0.9062; n_D^{20} 1.4190; Found MR 68.97; Calculated for $C_{13}H_{28}O_4$ MR 68.80.

$$\text{Found \%:} \quad C\ 62.80;\ H\ 11.04$$
$$C_{13}H_{28}O_4 \quad \text{Calculated \%:} \quad C\ 62.90;\ H\ 11.29$$

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

The procedure was similar to that of the preceding reactions. The chloro ether (30 g) was added dropwise to a solution of 18.7 g of sodium methoxide in 200 ml of absolute methanol. Heating was continued for 30 minutes. The product was 12.2 g of the bis(methoxymethyl) ether of 1,3-propanediol, b.p. 79° (16 mm); d_4^{20} 0.9946; n_D^{20} 1.4100; Found MR 40.85; Calculated for $C_7H_{16}O_4$ MR 41.09.

$$\text{Found \%:} \quad C\ 50.96;\ H\ 9.85$$
$$C_7H_{16}O_4 \quad \text{Calculated \%:} \quad C\ 51.22;\ H\ 9.75$$

In addition, 3.5 g of 1,3-propanediol was obtained. It had b.p. 98-100° at 8 mm; d_4^{20} 1.049; n_D^{20} 1.4370; Found MR 18.91; Calculated for $C_3H_8O_2$ MR 19.10.

Action of Sodium Ethoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

The bis(chloromethyl) ether of 1,3-propanediol (20 g) was added dropwise to a solution of 15.72 g of sodium ethoxide in 300 ml of absolute ethanol, and the mixture was heated in a water bath for 90 minutes. Sodium chloride was filtered off, and the filtrate was vacuum-fractionated, yielding the bis(ethoxymethyl) ether of 1,3-propanediol in 88.33% yield; it had b.p. 97-98.5° (14 mm); d_4^{20} 0.9470; n_D^{20} 1.4130; Found MR 50.55; Calculated for $C_9H_{20}O_4$ MR 50.33.

$$
\begin{array}{ll}
& \text{Found \%:} \quad C\ 56.13;\ H\ 10.54 \\
C_9H_{20}O_4 & \text{Calculated \%:} \quad C\ 56.25;\ H\ 10.41
\end{array}
$$

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

To 18.9 g of sodium isopropoxide, 20 g of the bis(chloromethyl) ether of 1,3-propanediol was added dropwise, and the mixture was heated in a water bath for one hour. Sodium chloride was filtered off, and the filtrate was fractionally distilled from a flask fitted with a Widmer column. The bis(isopropoxymethyl) ether of 1,3-propanediol was obtained in 70% yield; it had b.p. 106-109° (13 mm); d_4^{20} 0.9220; n_4^{20} 1.4160; Found MR 59.87; Calculated for $C_{11}H_{24}O_4$ MR 59.57.

$$
\begin{array}{ll}
& \text{Found \%:} \quad C\ 59.67;\ H\ 10.87 \\
C_{11}H_{24}O_4 & \text{Calculated \%:} \quad C\ 60.00;\ H\ 10.90
\end{array}
$$

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

The procedure followed that of the preceding reactions, 22.19 g of sodium butoxide, 350 ml of absolute butyl alcohol, and 20 g of the bis(chloromethyl) ether of 1,3-propanediol being taken. The products obtained were dibutoxymethane in 37.85% yield, b.p. 58° (8 mm); n_D^{20} 1.4090; and the bis(butoxymethyl) ether of 1,3-propanediol in 55.24% yield, b.p. 136-138° (9 mm); d_4^{20} 0.9199; n_D^{20} 1.4255; Found MR 69.00; Calculated for $C_{13}H_{28}O_4$ MR 68.81.

$$
\begin{array}{ll}
& \text{Found \%:} \quad C\ 63.17;\ H\ 11.25 \\
C_{13}H_{28}O_4 & \text{Calculated \%:} \quad C\ 62.90;\ H\ 11.29
\end{array}
$$

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of 1,3-Propanediol

The procedure followed that of the preceding reactions, the reactants being 15 g of the bis(chloromethyl) ether of 1,3-propanediol and 16.6 g of sodium isobutoxide in 250 ml of absolute isobutyl alcohol. The products isolated were 4.7 g of diisobutoxymethane, b.p. 160-161°; n_4^{20} 1.4010; and 13.7 g of the bis(isobutoxymethyl) ether of 1,3-propanediol, b.p. 120-123° at 8 mm; d_4^{20} 0.9117; n_D^{20} 1.4225; Found MR 69.19; Calculated for $C_{13}H_{28}O_4$ MR 68.81.

$$
\begin{array}{ll}
& \text{Found \%:} \quad C\ 62.87;\ H\ 11.07 \\
C_{13}H_{28}O_4 & \text{Calculated \%:} \quad C\ 62.90;\ H\ 11.29
\end{array}
$$

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

The reaction was carried out in a round-bottomed flask fitted with dropping funnel and reflux condenser. The bis(chloromethyl) ether of 1,3-butanediol (30 g) was added dropwise to 17.3 g of sodium methoxide in 200 ml of absolute methanol. The reaction was completed by heating the mixture in a water bath for one hour. The bis(methoxymethyl) ether of 1,3-butanediol was isolated in 64.9% yield; it had b.p. 79-80° (12 mm); d_4^{20} 0.9760; n_D^{20} 1.4120; Found MR 45.39; Calculated for $C_8H_{18}O_4$ MR 45.71.

$$
\begin{array}{ll}
& \text{Found \%:} \quad C\ 53.95;\ H\ 10.29 \\
C_8H_{18}O_4 & \text{Calculated \%:} \quad C\ 53.93;\ H\ 10.11
\end{array}
$$

Action of Sodium Ethoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

The reactants were 14.54 g of sodium ethoxide in 300 ml of absolute ethanol and 20 g of the bis(chloromethyl) ether of 1,3-butanediol. The bis(ethoxymethyl) ether of 1,3-butanediol was obtained in 45.4% yield; it had b.p. 101-102° (14 mm); d_4^{20} 0.9387; n_D^{20} 1.4148; Found MR 54.93; Calculated for $C_{10}H_{22}O_4$ MR 54.95.

$$
\begin{array}{ll}
& \text{Found \%:} \quad C\ 57.91;\ H\ 10.39 \\
C_{10}H_{22}O_4 & \text{Calculated \%:} \quad C\ 58.25;\ H\ 10.67
\end{array}
$$

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

To a solution of 17.54 g of sodium isopropoxide in 250 ml of absolute isopropyl alcohol, 20 g of the bis(chloromethyl) ether of 1,3-butanediol was added dropwise. The product isolated was 13.9 g of the bis(isopropoxymethl) ether of 1,3-butanediol, b.p. 113-116° (11 mm); d_4^{20} 0.9159; n_D^{20} 1.4170; Found MR 64.25; Calculated for $C_{12}H_{26}O_4$ MR 64.18.

$$C_{12}H_{26}O_4 \quad \begin{array}{l} \text{Found \%:} \quad \text{C 61.43; H 11.10} \\ \text{Calculated \%:} \quad \text{C 61.53; H 11.11} \end{array}$$

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

The procedure was similar to that of the preceding reactions, the reactants being 20.5 g of sodium butoxide, in 250 ml of absolute butyl alcohol and 20 g of the bis(chloromethyl) ether of 1,3-butanediol. The products isolated were 10.2 g of dibutoxymethane, b.p. 74.5-75.5° (17 mm); n_D^{20} 1.4085; and 9 g of the bis(butoxymethyl) ether of 1,3-butanediol, h.p. 152-154° (15 mm); d_4^{20} 0.9163; n_D^{20} 1.4260; Found MR 73.26; Calculated at $C_{14}H_{30}O_4$ MR 73.42.

$$C_{14}H_{30}O_4 \quad \begin{array}{l} \text{Found \%:} \quad \text{C 63.81; H 11.22} \\ \text{Calculated \%:} \quad \text{C 64.12; H 11.45} \end{array}$$

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of 1,3-Butanediol

The reaction was carried out as usual, the reactants being 20.5 g of sodium isobutoxide and 20 g of the bis(chloromethyl) ether of 1,3-butanediol. The products isolated were 4.5 g of diisobutoxymethane, b.p. 160°; n_D^{20} 1.4030; and 20.2 g of the bis(isobutoxymethyl) ether of 1,3-butanediol, b.p. 130-131.5° (8.5 mm); d_4^{20} 0.9064; n_D^{20} 1.4235; Found MR 73.68; Calculated for $C_{14}H_{30}O_4$ MR 73.42.

$$C_{14}H_{30}O_4 \quad \begin{array}{l} \text{Found \%:} \quad \text{C 63.99; H 11.35} \\ \text{Calculated \%:} \quad \text{C 64.12; H 11.45} \end{array}$$

Action of Sodium Methoxide on the Bis(chloromethyl) Ether of 2-Butyne-1,4-diol

The reaction was carried out as usual, the reactants being 8.85 g of sodium methoxide in 150 ml of absolute methanol and 15 g of the bis(chloromethyl) ether of 2-butyne-1,4-diol. The bis(methoxymethyl) ether of 2-butyne-1,4-diol was obtained in 89.43% yield; it had b.p. 114-116° (11 mm); d_4^{20} 1.0493; n_D^{20} 1.4417; Found MR 43.85; Calculated for $C_8H_{14}O_4$ MR 43.71.

$$C_8H_{14}O_4 \quad \begin{array}{l} \text{Found \%:} \quad \text{C 54.64; H 7.76} \\ \text{Calculated \%:} \quad \text{C 55.17; H 8.04} \end{array}$$

Action of Sodium Isopropoxide on the Bis(chloromethyl) Ether of 2-Butyne-1,4-diol

The reactants were 13.4 g of sodium isopropoxide in 200 ml of absolute isopropyl alcohol and 15 g of the bis(chloromethyl) ether in 2-butyne-1,4-diol. The product isolated was 7.3 g of the required bis(isopropoxymethyl) ether of 2-butyne-1,4-diol, b.p. 138-140° (13.5 mm); d_4^{20} 0.9748; n_D^{20} 1.4398; Found MR 62.16; Calculated for $C_{12}H_{22}O_4$ MR 62.18.

$$C_{12}H_{22}O_4 \quad \begin{array}{l} \text{Found \%:} \quad \text{C 61.99; H 9.45} \\ \text{Calculated \%:} \quad \text{C 62.17; H 9.56} \end{array}$$

Action of Sodium Butoxide on the Bis(chloromethyl) Ether of 2-Butyne-1,4-diol

The reactants were 15.7 g of sodium butoxide in 200 ml of absolute butyl alcohol and 15 g of the chloro ether. It was found possible, after several fractionations, to isolate 1.7 g of dibutoxymethane, b.p. 55-58° (6 mm); and 13.2 g of the bis(butoxymethyl) ether of 2-butyne-1,4-diol, b.p. 155-158° (6 mm); d_4^{20} 0.9574; n_D^{20} 1.4437; Found MR 71.53; Calculated for $C_{14}H_{26}O_4$ MR 71.39.

$$C_{14}H_{26}O_4 \quad \begin{array}{l} \text{Found \%:} \quad \text{C 64.87; H 9.89} \\ \text{Calculated \%:} \quad \text{C 65.11; H 10.00} \end{array}$$

Action of Sodium Isobutoxide on the Bis(chloromethyl) Ether of 2-Butyne-1,4-diol

The chloro ether (15 g) was added dropwise to a solution of 15.7 g of sodium isobutoxide in 200 ml of absolute isobutyl alcohol. The products isolated were 2 g of diisobutylmethane, b.p. 159-161°; n_D^{20} 1.4005; and 17.7 g of the bis(isobutoxymethyl) ether of 2-butyne-1,4-diol, b.p. 145° (6 mm); d_4^{20} 0.9506; n_D^{20} 1.4400; Found MR 71.53; calculated at $C_{14}H_{26}O_4$ MR 71.39.

$$C_{14}H_{26}O_4 \quad \begin{array}{l} \text{Found \%:} \quad \text{C 65.36; H 9.68} \\ \text{Calculated \%:} \quad \text{C 65.11; H 10.04} \end{array}$$

Alcoholysis of the Bis(ethoxymethyl) Ether of 1,3-Propanediol

A solution of sodium ethoxide obtained by dissolving 0.1 g of sodium in 40 ml of absolute ethanol was introduced into a round-bottomed flask fitted with reflux condenser, and 8 g of the bis(ethoxymethyl) ether of 1,3-propanediol was added. The mixture was heated in an oil bath for four hours. Fractionation: yield 35 ml of a substance of b.p. 73-112° and 6 g of a substance of b.p. 91° (11 mm) and n_D^{25} 1.4125; the residue was 3.2 g. The boiling point and refractive index of the second substance indicates that it is the bis(ethoxymethyl) ether of 1,3-propanediol. No alcoholysis products were detected in this case.

Alcoholysis of the Bis(butoxymethyl) Ether of Ethylene Glycol

A mixture of 100 ml of absolute butyl alcohol, 4.1 g of the bis(butoxymethyl) ether of ethylene glycol, and 2-3 drops of the bis(chloromethyl) ether of ethylene glycol was heated for four hours. Fractionation of the reaction products from an Arubzov flask gave 2.7 g of material of b.p. 59-62° (10 mm); n_D^{25} 1.4058; d_4^{25} 0.8334; and 0.8 g of material of b.p. 85-92° (10 mm); n_D^{26} 1.4220.

The substance of b.p. 59-62° (10 mm) corresponded to dibutoxymethane. The product of b.p. 88-92° (10 mm) was probably the monoether of ethylene glycol. We did not succeed in isolating any of the bis(butoxymethyl) ether.

Alcoholysis of the Bis(butoxymethyl) Ether of 1,2-Propanediol

A mixture of 4.7 g of the 1,2-propanediol ether and 100 ml of butyl alcohol was placed in a round-bottomed flask fitted with reflux condenser, and two drops of the bis(chloromethyl) ether of 1,2-propanediol were added. The mixture was heated at the boiling point of the alcohol for three hours. Fractionation of the reaction products yielded butyl alcohol and also 2.1 g of dibutoxymethane, b.p. 60-63° (9 mm); n_D^{20} 1.4060.

Alcoholysis of the Bis(isobutoxymethyl) Ether of 1,3-Butanediol in Weakly Alkaline and Acid Media

Experiment 1. A mixture of a solution of sodium isobutoxide prepared by dissolving 0.1 g of sodium in 70 ml of isobutyl alcohol and 10.3 g of the bis(isobutoxymethyl) ether of 1,3-butanediol was heated at 106° for four hours. Fractionation yielded isobutyl alcohol and 9 g of the bis(isobutoxymethyl) ether of 1,3-butanediol, b.p. 132-134° (9.5 mm). In this case, therefore, no alcoholysis of the ether occurred.

Experiment 2. When a mixture of 70 ml of isobutyl alcohol, 8 g of the bis(isobutoxymethyl) ether of 1,3-butanediol and two drops of the bis(chloromethyl) ether of 1,3-butanediol was heated, alcoholysis of the ether was observed. Fractionation of the alcoholysis products yielded isobutyl alcohol and diisobutoxymethane, b.p. 162-165° and n_D^{25} 1.4010. The literature gives b.p. 164.3°, n_D^{20} 1.4020 [12].

SUMMARY

1. A study has been made of the chloromethylation of 1,2- and 1,3-propanediols, and this has resulted in the preparation of the two corresponding bis(chloromethyl) ethers, which have not been described previously.

2. A study has been made of the reactions of the bis(chloromethyl) ethers of ethylene glycol, 1,2- and 1,3-propanediols, 1,3-butanediol and 2-butyne-1,4-diol with the methoxide, ethoxide, isopropoxide, butoxide, and isobutoxide of sodium. These reactions have resulted in the preparation of the corresponding bis(alkoxymethyl) ethers of the glycols and also the mono(isopropoxymethyl) and mono(isobutoxymethyl) ethers of ethylene glycol, the mono(butoxymethyl) ether of 1,2-propanediol, and the compound $C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9$

3. It has been established that in the reactions of all of the investigated bis(chloromethyl) ethers of glycols with sodium butoxide and with sodium isobutoxide, by-products, i.e., dibutoxymethane and diisobutoxymethane, are formed. Also, in the reactions of the bis(chloromethyl) ether of ethylene glycol with sodium isobutoxide and of the bis(chloromethyl) ether of 1,2-propanediol with sodium butoxide, not only the corresponding acetals and bis(alkoxymethyl) ethers were formed, but also the corresponding mono(alkoxymethyl) ethers of these glycols. As a result of the reaction of the bis(chloromethyl) ether of ethylene glycol with sodium butoxide, in addition to dibutoxymethane and the bis(butoxymethyl) ether of the glycol, the following compound

was obtained:

$$C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9$$
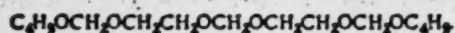
4. Hypotheses have been advanced in explanation of the formation of the acetals, monoethers of the glycols, and the substance

$$C_4H_9OCH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2OC_4H_9$$
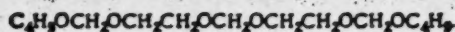
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ISOMERIZATION OF TERPENE HYDROCARBONS BY THE ACTION OF SILICA GEL

UNDER THE CONDITIONS OF ADSORPTIONAL ANALYSIS

B. A. Arbuzov and Z. G. Isaeva

In terpene chemistry the chromatographic method began to be adopted at the beginning of the thirties of this century, and the method is now fairly widely applied in the study of mono-, sesqui-, di-, and tri-terpenes [1-11]. The sorbent generally used for the chromatography of terpene compounds is aluminum oxide, although other sorbents have been used, e.g. activated charcoal and, very rarely, silica gel. The main, determining factor in the application of one or other sorbent is its chemical inertness toward the substances to be chromatographed, but the majority of substances that are used as sorbents are active catalysts for reactions of isomerization, polymerization, oxidation, splitting, etc. There are numerous examples in the literature of the catalytic action of sorbents on substances undergoing separation [12].

In 1951 we began an investigation of the behavior of some terpene hydrocarbons on silica gel under the conditions of adsorptional analysis, with the object of determining the possibility of applying silica gel to the chromatographic separation of mixtures of terpene compounds. In a study of the behavior of separate terpene hydrocarbons toward silica gel, we found that, under the conditions of adsorptional analysis, a-pinene, Δ^3-carene, and dipentene are isomerized by silica gel. Among the isomerization products of a-pinene we found camphene, dipentene, and terpinolene, and among the isomerization products of dipentene, terpinolene and p-cymene were identified. Δ^3-Carene isomerized into dipentene, and via dipentene into terpinolene. The action of silica gel on a-pinene, Δ^3-carene, and dipentene was thus found to be analogous to the action of activated clays on these substances, a thorough investigation of which has been made by Tishchenko, Rudakov, and others.

The isomerization of terpene hydrocarbons under the action of clays was first observed by Gurvich [13] in 1915, who observed the isomerization of a-pinene in presence of fuller's earth: among the reaction products, together with a large amount of polyterpenes, he found camphene and traces of monocyclic terpenes. Tishchenko and Marga [14] confirmed Gurvich's results. Similar results were obtained by Tsutomu Kuvata [15] by the action of acidic Japanese clays on pinene. Venable [16] found, in 1932, that a-terpinene was formed when dipentene was heated with fuller's earth.

In 1933, Tishchenko and Rudakov [17], in a study of the action of various active clays on a-pinene, found the optimum conditions for the preparation of camphene in high yield. This reaction was later studied by Rudakov [15] in greater detail, and among the reaction products camphene (50-55%), fenchene (5-6%), monocyclic terpenes (30-40%), and polymers (5-10%) were found. Dipentene, according to Rudakov's results [18], is isomerized under the action of activated clay into terpinolene, which is then converted into a-terpinene under the action of the same catalyst; also, p-cymene, p-menthene, and polymers are formed in the reaction. Among the products formed during the isomerization of Δ^3-carene under the same conditions, dipentene, terpinolene, sylvestrene in very small amount, and polymers were found [19].

When camphene is heated in presence of activated clay, the main reaction products are polyterpenes; p-cymene and borneol were identified among the products [20]. The isomerization of terpene hydrocarbons was performed by Rudakov and coworkers at high temperatures, 160-180°. Hence, the isomerization of a-pinene, Δ^3-carene, and dipentene on silica gel under the conditions of adsorptional analysis is analogous to that occurring on activated clays, but considerably milder temperature conditions are required (6-10°).

a-Pinene, when passed through a silica-gel column, gave a mixture of reaction products, which was separated into 18 fractions by fractionation through a 24-plate column. The results are summarized in Table 1 and are presented graphically in Fig. 1. The fractions of zone A, which formed 10% by weight of the reaction products, consisted essentially of camphene; we did not establish the nature of the impurities present. The fractions of zone B (4.7%) consisted of pure camphene. The fractions of zone D consisted of dipentene. Zone C was an intermediate

Table 1

Fraction No	B.p. in °C (pressure in mm Hg)		Weight (g)	n_D^{20}	d_4^{20}	Yield (%)
I	52.5-53	(21)	5.8	1.4618	0.8656	1.63
II	53-54	(21)	13	1.4635	0.8657	3.67
III	54-54.5	(21)	11.9	1.4665	0.8653	3.37
IV	53-53.5	(19)	9.5	1.4684	0.8640	2.68
V	50.5-52	(12)	29	Crystal	—	8.98
VI	57.5	(22)	16.8	•	—	4.76
VII	59	(23)	86	•	—	24.29
VIII	63.5	(27)	9.7	•	—	2.74
IX	63.5-66	(27)	4.5	•	—	1.27
X	64-76	(25)	13.3	1.4730	0.8492	3.75
XI	76-76.5	(25)	35.9	1.4740	0.8419	10.15
XII	68	(17.5)	16.5	1.4727	0.8466	4.66
XIII	58	(12)	19.9	1.4733	0.8445	5.62
XIV	44	(7.5)	23.5	1.4720	0.8426	6.64
XV	41.5-44	(6.5)	10.7	1.4840	0.8545	3.02
XVI	44-45.5	(6.5)	13.1	1.4830	0.8556	3.71
XVII	45.5-47.5	(6.5)	12.9	1.4890	0.8822	3.65
	Residue		22	—	—	6.22

Fig. 1

fraction, terpinolene formed 9% of the reaction products (zone E), and the residue (6%) was not investigated. Dipentene and terpinolene were identified by preparing their tetrabromides. Terpinolene is an isomerization product of dipentene, as was shown by a special experiment.

These results on the behavior of a-pinene on silica gel are in conflict with the statement of Tishchenko and Rudakov [17] concerning the indifference of "samples of highly active silica gel" toward pinene, which they made in the course of a discussion of the mechanism of the isomerizing action of various clays on pinene.

The results obtained in the study of the action of silica gel on dipentene under the conditions of adsorptional analysis are given in Table 2 and presented graphically in Fig. 2. As will be seen from Table 2, the isomerization of dipentene with silica gel yields a complex mixture of reaction products.
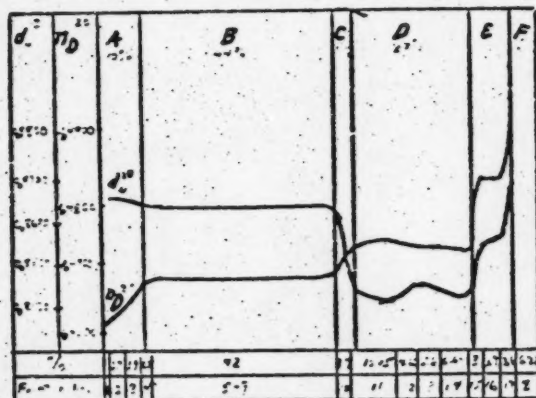
Among the components of the fractions of zone A (16% by weight of the reaction products) were a small amount of p-cymene (identified by oxidation with chromic anhydride to terephthalic acid and the preparation from the latter of its dimethyl ester) and a product that polymerized when treated with sulfuric acid. The constants of Fraction II, which formed the bulk of zone A, were close to those of a-terpinene (b.p. 173.5-174.8° (755 mm); $d_4^{19.7}$ 0.8375, n_D^{19} 1.477). The substance of b.p. 57.5° (12 mm), however, gave no derivatives of a-terpinene: we did not succeed in preparing the maleic anhydride adduct of a-terpinene, nor the nitrosite of a-terpinene, and the nature of this substance (Fraction II) was not established. Zone B (34%) was unchanged dipentene: Fractions III and VII gave dipentene tetrabromide, m.p. 122-123° when brominated. Fractions of zone D contained terpinolene, identified by the preparation of its tetrabromide, m.p. 116-116.5°. The fractions of zone E and the residue remaining after the distillation were not investigated further.

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These results show that under the conditions of adsorptional analysis, silica gel isomerizes dipentene into terpinolene, which undergoes further transformations, some idea of which can be formed from the fact that p-cymene was found among the reaction products.
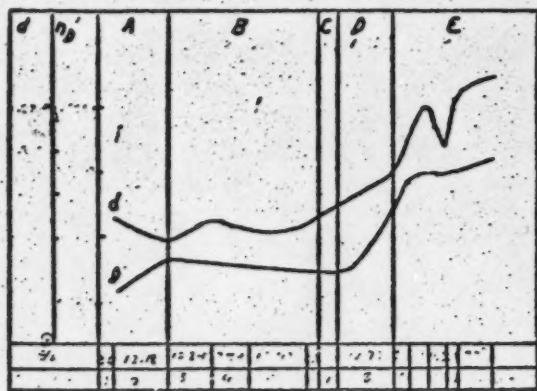

Fig. 2.

The results of the study of the action of silica gel on Δ³-carene under the conditions of adsorptional analysis are presented in Table 3 and Fig. 3, from which it will be seen that only 37% isomerization occurs. The fractions of zones A and B contained unchanged carene, and zone C contains intermediate fractions. The main component of the fractions of zone D (13% of the reaction products) was dipentene: bromination of these fractions yielded the tetrabromide, m.p. 122-123°. Fraction XII, represented in Fig. 3 by zone E (2%), contained terpinolene, which, as shown above, is formed by the isomerization of dipentene. The tetrabromide obtained from Fraction XII melted at 115-116°. The composition of the fractions making up zones F and G was not investigated.

TABLE 2

Fraction No.	B p. in °C (pressure in mm Hg)	Weight (g)	n_D^{20}	d_4^{20}	Yield (%)
I	54-57.5 (12.5)	4.5	1.4720	0.8451	3.57
II	57.5 (12)	15.7	1.4772	0.8395	12.18
III	56.5-57 (11.5)	13.2	1.4763	0.8449	10.24
IV	53.5 (10)	10.3	1.4760	0.8424	7.99
V	45 (7)	17.3	1.4753	0.8429	13.41
VI	40.5-42 (6)	3.6	1.4753	0.8461	2.79
VII	42-45 (6)	5.3	1.4750	0.8475	4.11
VIII	45-48 (6)	16.4	1.4838	0.8551	12.72
IX	59.5-61 (6)	5.1	1.4893	0.8652	3.96
X	65-66 (8)	5.2	1.4900	0.8713	4.03
XI	66 (8)	5.5	1.4897	0.8608	4.27
XII	63.5 (7.5)	2.7	1.4905	0.8732	2.10
XIII	63.5-65 (7)	10	1.4922	0.8768	7.76
Residue		14	(viscous liquid)		

EXPERIMENTAL

The terpene hydrocarbons employed for the investigation of the behavior of such substances on silica gel under the conditions of adsorptional analysis, a-pinene, Δ³-carene, and dipentene, were passed through a water-cooled silica-gel column. The height of the column was 1500 mm, and with respect to diameter the column was divided into three parts: the diameter was 12 mm in the lower part, 24 mm in the middle part, and 39 mm in the upper part. The silica gel was contained in the lower and middle parts of the column. The activity of the silica gel with respect to benzene was 9-11 ml. The weight ratios of terpene hydrocarbons and silica gel are given below for each separate case. For the elution of the hydrocarbons from the adsorbent, alcohol and water were used.

Isomerization of a-Pinene

Pinene [b.p. 40° (12 mm); n_D^{20} 1.4650; d_4^{20} 0.8596], separated from sulfate turpentine by fractionation through a 24-plate column, was passed through a silica-gel column. The activity of the silica gel with respect to benzene was 9.48 ml. The weight ratio of pinene to silica gel was 1 : 1.5. The catalyzate from four experiments (379 g) was fractionated twice through a 24-plate column, and the results are given in Table 1.

Bromination of the Fraction of b.p. 64-76° (25 mm)

A solution of 2 g of the substance of b.p. 64-76° (25 mm) in 7 ml of dry ether and 5 ml of amyl alcohol was added dropwise to a solution of 2 ml of bromine in 10 ml of dry ether, which was cooled with snow. The precipitate was crystallized from alcohol; m.p. 115-117°; after a second crystallization from alcohol, m.p. 122-122.5°;

Table 3

Fraction No	B p in °C (pressure in mm Hg)	Weight (g)	n_D^{20}	d_4^{20}	Yield (%)
I	41.5 (8)	12.8	1.4740	0.8586	6.12
II	46.5 (8.5)	11.9	1.4730	0.8596	5.69
III	46.5–47 (8.5)	6.3	1.4730	0.8604	3.01
IV	52–53 (11)	16.3	1.4727	0.8607	7.8
V	56.5 (13)	15.1	1.4726	0.8612	7.22
VI	58 (14)	5.4	1.4726	0.8612	2.58
VII	59 (14.5)	27.8	1.4720	0.8612	13.30
VIII	60.5 (16)	25.8	1.4720	0.8615	12.34
IX	65.5 (19)	23	1.4737	0.8564	11.00
X	66 (17.5)	22.3	1.4740	0.8440	10.67
XI	50 (8)	5.9	1.4740	0.8421	2.82
XII	46.5–48 (6.5)	5.5	1.4878	0.8579	2.63
XIII	47.5–48 (6)	5.1	1.5033	0.8653	2.44
Residue		25.8			12.34

Fig. 3

after a third, m.p. 122-123°. A mixture test with dipentene tetrabromide showed no depression of melting point.

Bromination of the Fraction of b.p. 44° (7.5 mm)

The tetrabromide was prepared from 2 g of the substance of b.p. 44° (7.5 mm), 2 ml of bromine, 17 ml of ether, and 5 ml of amyl alcohol, and after three crystallizations from ethanol it melted at 121-122°. A mixture with dipentene dibromide melted at 121-122°.

Bromination of the Fraction of b.p. 41.5-44° (6.5 mm)

A solution of 2 g of the substance of b.p. 41.5-44° (6.5 mm) in 7 ml of ether and 5 ml of amyl alcohol was added to a cooled and constantly stirred solution of 3 ml of bromine in 10 ml of dry ether. Toward the end of the addition, a precipitate formed, the melting point of which after the first crystallization from alcohol was 106-111° (1.3 g). After the second crystallization from alcohol the melting point was 111-114° (0.9 g). After a third, it was 115-116° (0.5 g). The melting point of terpinolene tetrabromide is 116°.

Investigation of the Camphene Fraction, B.p. 52.5-53° (21 mm)

A mixture of 3.1 g of the substance of b.p. 52.5-53° (21 mm), 10 g of glacial acetic acid, and 0.3 g of sulfuric acid (sp.gr. 1.82) was heated in a water bath for 2 hours 30 minutes. The reaction mixture was cooled and poured into water; the upper layer was separated, washed with water, and hydrolyzed with a solution of 2 g of KOH in 15 ml of ethanol, the mixture being heated in a water bath for two hours. When the reaction mixture was poured into water, a resinous layer separated, and filtration yielded a small
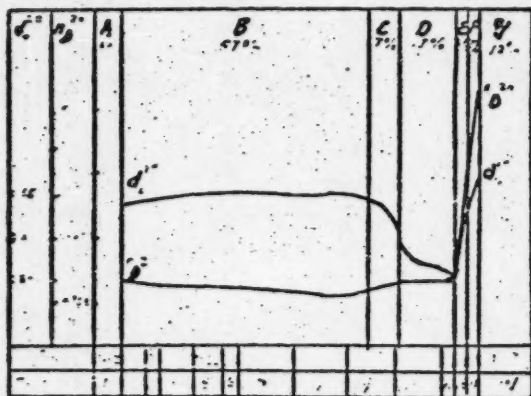
amount of substance, which was pressed off on filter paper and air-dried. It melted at 175-190° in a sealed capillary. It was readily soluble in the cold in alcohol, ether, and acetone. Melting point after recrystallization from gasoline, 194-197°. The weight of substance was 2.2 g (62.8% yield of isoborneol). The melting point of isoborneol from the Ural works was 193-199°, after recrystallization from gasoline of b.p. up to 130°. The peak on the specific gravity curve (Fig. 1, zone D) was caused by the high specific gravity of Fraction XII, as compared with Fractions XI and XIII, which consisted of dipentene. The residue remaining after distillation of the catalyzate was not investigated.

Isomerization of Dipentene.

Catalyzate (140 ml) obtained by passage of dipentene [b.p. 65° (15 mm); n_D^{20} 1.4730; d_4^{20} 0.8420] through a silica-gel column (activity of silica gel 11 ml) was fractionated through a 24-plate column into 14 fractions. The weight ratio of dipentene to silica gel was 1 : 1.4. The dimensions of the silica-gel column are given above. The results of the fractionation are given in Table 2.

Treatment of the Fraction of B.p. 57.5° (12 mm) with Sulfuric Acid.

The substance (3 ml) was shaken in a 10-ml cylinder with three portions of 70% sulfuric acid and then with a portion of 80% sulfuric acid, when the upper layer attained a constant volume of 1.9 ml. The upper layer (reddish brown) was separated, neutralized with a solution of sodium carbonate, washed with water, and extracted with ether. The ether extracts were dried with calcined potassium carbonate, the ether was driven off, and the residue was vacuum distilled, yielding the fractions:

Fraction I, b.p. 55-57° (4.5 mm); 0.1 g; n_D^{20} 1.4824 (odor of cymene)
Fraction II, b.p. 140-150° (4 mm); 1 g; n_D^{20} 1.5155 (viscous liquid)

Oxidation of the Substance of b.p. 57.5° (12 mm) with Chromic Anhydride.

The substances taken for reaction were 2.1 g of the substance of b.p. 57.5° (12 mm), 10 g of chromic anhydride, 20 ml of 60% acetic acid, 10 ml of water, and 9 ml of sulfuric acid (sp.gr. 1.8). The substance was added carefully, with snow cooling, to a mixture of the remaining reaction components, and the resulting mixture was boiled gently for six hours. The mixture was cooled and poured into water, and the precipitate that formed was filtered off and dried; weight 0.03 g.

Preparation of Dimethyl Terephthalate.

A mixture of 0.03 g of terephthalic acid, obtained by the oxidation of the substance of b.p. 57.5° (12 mm), 5 ml of methanol, and 0.5 ml of sulfuric acid (sp.gr. 1.8) was boiled for five hours. The mixture was cooled and poured into water, and the flocs that were precipitated were filtered off, dried (weight 0.02 g), and crystallized from methanol; m.p. 137-139°. The substance of b.p. 57.5° (12 mm) gave no adduct with maleic anhydride. Bromination of Fractions III and VII yielded a tetrabromide of m.p. 122-123°.

Bromination of the Fraction of B.p. 45-48° (6 mm).

A solution of 5 g of the substance of b.p. 45-48° (6 mm) in 10 ml of ether and 8 ml of amyl alcohol was added to a cooled and constantly stirred solution of 5 ml of bromine in 25 ml of dry ether. After some time a precipitate formed; it was filtered off and crystallized from alcohol; weight 2.85 g, m.p. 115°. After a second crystallization, m.p. 116-116.5°.

Isomerization of Δ³-Carene

Δ³-Carene [b.p. 54° (12 mm); n_D^{20} 1.4730; d_4^{20} 0.8612] was passed twice through a silica-gel column (activity of silica gel 9.04 ml). The weight ratio of Δ³-carene to silica gel was 1 : 2. Fractionation of 219 g of catalyzate through a 24-plate column yielded the fractions given in Table 3. The substance of b.p. 65.5° (19 mm) did not give dipentene tetrabromide when brominated.

Bromination of the Fraction of B.p. 66° (17.5 mm).

A solution of 2 g of the substance in 7 ml of ether and 5 ml of amyl alcohol was added to a cooled (snow and salt) and constantly stirred solution of 2 ml of bromine in 10 ml of ether. By the next day a crystalline precipitate had formed. It was filtered off and air-dried; weight 2.8 g. After two crystallizations from alcohol: m.p. 122-123°; weight 1.6 g. A mixture test with the tetrabromide obtained from dipentene showed no depression of melting point.

Bromination of the Fraction of B.p. 46.5-48° (6.5 mm).

The substances taken for reaction were 1.8 g of the substance of b.p. 46.5-48° (6.5 mm), 2.1 g of bromine, 19 ml of ether, and 4 ml of amyl alcohol. The procedure was similar to that described above. The melting point of the tetrabromide was 113-114° after the first crystallization and 115-116° after the second. The residue remaining after distillation of the catalyzate was not investigated.

SUMMARY

1. α-Pinene, Δ³-carene, and dipentene are isomerized on silica gel under the conditions of adsorptional analysis: α-pinene is isomerized to camphene, dipentene, and terpinolene; Δ³-carene to dipentene and terpinolene; and dipentene to terpinolene, which then undergoes further transformation. In the first two cases the terpinolene is formed by the isomerization of dipentene.

2. The isomerization of α-pinene, Δ³-carene, and dipentene by silica gel under the conditions of adsorptional analysis is analogous to their isomerization by activated clays at temperatures close to the boiling points

of the hydrocarbons.

3. The results obtained for the isomerization of α-pinene by silica gel under the conditions of adsorptional analysis do not accord with the assertion by Tishchenko and Rudakov concerning the indifference of "samples of highly active silica gel" with respect to pinene.

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and

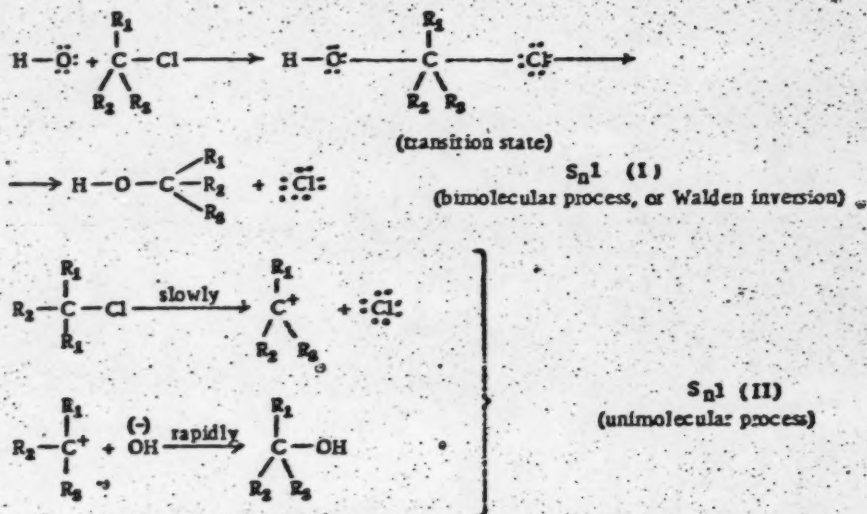V. I. Ulyanov-Lenin Kazan State University

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OPTICALLY ACTIVE ORGANOMERCURY COMPOUNDS

COMMUNICATION 2. MECHANISM OF ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

### A. N. Nesmeyanov, O. A. Reutov, and S. S. Poddubnaya

The mechanism of nucleophilic substitution in the aliphatic series has been the subject of a large number of investigations. The results of numerous investigations, mainly on the kinetics of the hydrolysis of alkyl halides, led Ingold, Hughes, and coworkers [1] to the conclusion that there exist two different mechanisms for nucleophilic substitution at a saturated carbon atom:

(transition state)

S_n1 (I)
(bimolecular process, or Walden inversion)

S_n1 (II)
(unimolecular process)

Swain [2] has recently confirmed the existence of two mechanisms for the hydrolysis of alkyl halides, but showed that the course of the hydrolysis was more complex, being in each case a termolecular process (reaction proceeds when, and only when, a carbon and the halogen attached to it are attacked simultaneously). Hence, an intensive study of the hydrolysis of alkyl halides has resulted in the elucidation of the mechanism of nucleophilic substitution at a saturated carbon atom.
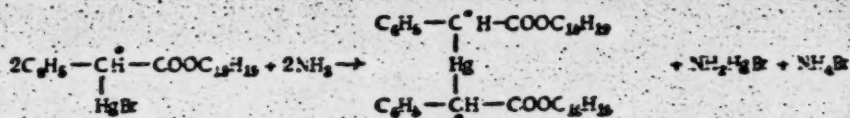
At yet, however, there are no experimental facts known that would allow us to obtain an idea of the mechanism of electrophilic substitution at a saturated carbon atom, or, in particular, of its stereochemical course (inversion, racemization, maintenance of configuration?). The object of the present work was the investigation of the stereochemistry of electrophilic substitution at a saturated carbon atom.

As an object for investigation we have chosen the electrophilic substitution reaction occurring when mercuric bromide reacts with the di(−)-menthyl ester of mercuribis(phenylacetic acid):
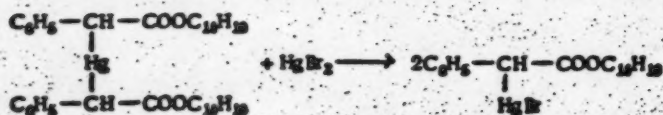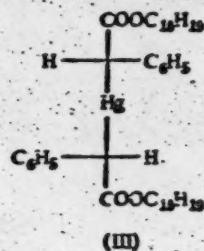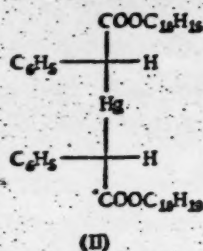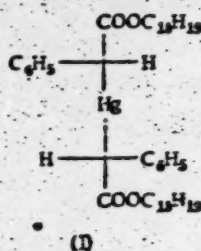
The symmetrical organomercury compounds that we required were obtained by the symmetrization of the pure diastereoisomeric (−)-menthyl esters of (bromomercuri)phenylacetic acid, the syntheses of which have been described in the preceding communication [3]. In the course of the preparation of the symmetrical starting compounds it was found to be necessary, and also possible, to solve the question of the mechanism of the symmetrization of organomercury compounds of the aliphatic series under the action of ammonia.

In the symmetrization of one of the diastereoisomers of the (−)-menthyl ester of (bromomercuri)phenylacetic acid

$$2C_6H_5-\overset{\bullet}{C}H-COOC_{10}H_{19} + 2NH_3 \rightarrow \quad \begin{matrix} C_6H_5-\overset{\bullet}{C}H-COOC_{10}H_{19} \\ | \\ Hg \\ | \\ C_6H_5-\overset{\bullet}{C}H-COOC_{10}H_{19} \end{matrix} \quad + NH_2HgBr + NH_4Br$$

the formation of the following isomers of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] are formally possible:
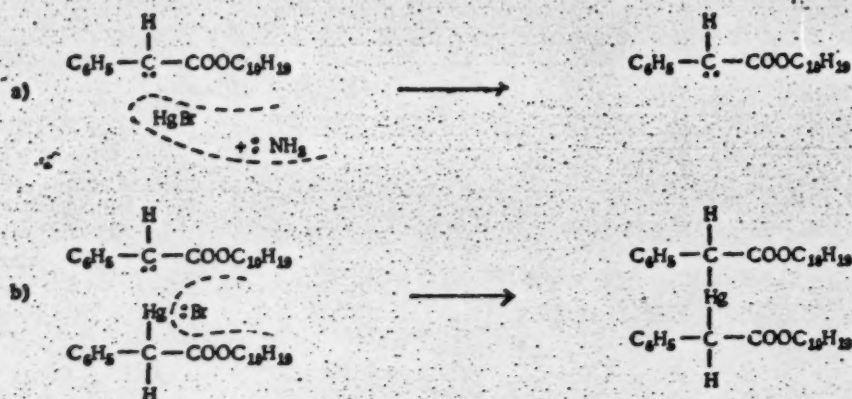

(I) (II) (III)

1. If symmetrization is accompanied by preservation of the configuration of the asymmetrical carbon atoms in both molecules of the original substance, then only one isomer of the final symmetrical organomercury compound (I or III according to the configuration of the starting substance) can be formed.

2. If symmetrization is accompanied by preservation of the configuration of one molecule of the starting substance and racemization of the second molecule, then two isomers (I and II, or II and III, according to the configuration of the starting substance) can be formed.

3. If symmetrization is accompanied by preservation of the configuration of one molecule of the starting substance and inversion of the configuration of the second molecule, then only one isomer can be formed (II, irrespective of the configuration of the starting substance).

4. If symmetrization is accompanied by inversion of the configuration of one molecule of the starting substance and racemization of the second molecule, then two isomers (II and III, or I and II, according to the configuration of the starting substance) can be formed.

5. If symmetrization is accompanied by inversion of the configurations of both molecules of the starting substance, then only one isomer (III or I according to the configuration of the starting substance) can be formed.

6. If symmetrization is accompanied by racemization of both molecules, then, irrespective of the configuration of the molecules of the starting substance, all three possible isomers of the final symmetrical organomercury compound must be formed.

Symmetrization of the (−)-menthyl ester of (bromomercuri)phenylacetic acid of $[\alpha]_D^{18} -95°$ and m.p. 161-162° (diastereoisomer I) results in the formation of one single isomer of the symmetrical organomercury compound, $[\alpha]_D^{18} -21.4°$ and m.p. 119-122°. Symmetrization of the (−)-menthyl ester of (bromomercuri)phenylacetic acid of $[\alpha]_D^{18} -49.3°$ and m.p. 152-154° (diastereoisomer II) results in the formation of a single but different isomer of the symmetrical organomercury compound, having $[\alpha]_D^{18} -7.7°$ and m.p. 118-120°.

Variants 2, 4, and 6 are therefore eliminated, being in conflict with the fact of the formation of only one stereoisomer of the symmetrical organomercury compound. The fifth variant is impossible because the asymmetrical carbon atom of only one of the original molecules of organomercury salt is affected in the symmetrization. The third variant is eliminated by the fact that it would require the formation of the same isomer of the symmetrical organomercury compound in the symmetrization both of diastereoisomer I and of diastereoisomer II.

We must therefore conclude that symmetrization is accompanied by the preservation of the configurations of asymmetrical carbon atoms in both molecules of the original substance* (variant I). The symmetrization reaction may be represented as follows**:
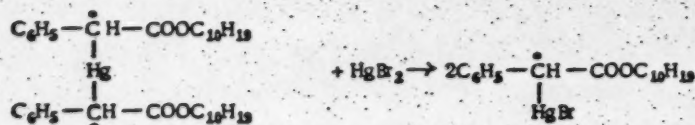
a)
$$C_6H_5 - \overset{\overset{H}{|}}{\underset{|}{C}} - COOC_{10}H_{19}$$
HgBr
$$+ : NH_2$$
$$\longrightarrow$$
$$C_6H_5 - \overset{\overset{H}{|}}{\underset{|}{C}} - COOC_{10}H_{19}$$

b)
$$C_6H_5 - \overset{\overset{H}{|}}{\underset{|}{C}} - COOC_{10}H_{19}$$
Hg : Br
$$C_6H_5 - \overset{|}{\underset{\underset{H}{|}}{C}} - COOC_{10}H_{19}$$
$$\longrightarrow$$
$$C_6H_5 - \overset{\overset{H}{|}}{\underset{|}{C}} - COOC_{10}H_{19}$$
Hg
$$C_6H_5 - \overset{|}{\underset{\underset{H}{|}}{C}} - COOC_{10}H_{19}$$

In this case, therefore, the electrophilic replacement

$$(R - HgBr + R - HgBr \overset{NH_3}{\longrightarrow} R - Hg - R)$$
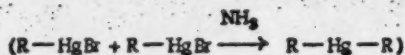
occurs with preservation of the configuration of the asymmetrical carbon atom.

As far as we have been able to discover from the literature, the mechanism of the symmetrization reaction has never been investigated: this is the first paper in this field. In all probability, the stereochemical course of the symmetrization of organomercury compounds of the aliphatic series under the action of alkali-metal alkoxides, alkali-metal cyanides and thiocyanates, hydrazine, and other nucleophilic reagents will be similar to that of the reactions we have investigated.

As we now had pure diasteriomeric di-(−)-menthyl esters of mercuribis[phenylacetic acid] (obtained by the symmetrization of the pure diastereoisomers of the (−)-menthyl ester of (bromomercuri)phenylacetic acid), we were able to study the reactions of these substances with mercuric bromide, which are electrophilic substitution reactions:***

$$C_6H_5 - \overset{\overset{\bullet}{|}}{\underset{|}{C}H} - COOC_{10}H_{19}$$
Hg
$$C_6H_5 - \overset{|}{\underset{}{C}H} - COOC_{10}H_{19}$$
$$+ HgBr_2 \rightarrow 2C_6H_5 - \overset{\overset{\bullet}{|}}{\underset{|}{C}H} - COOC_{10}H_{19}$$
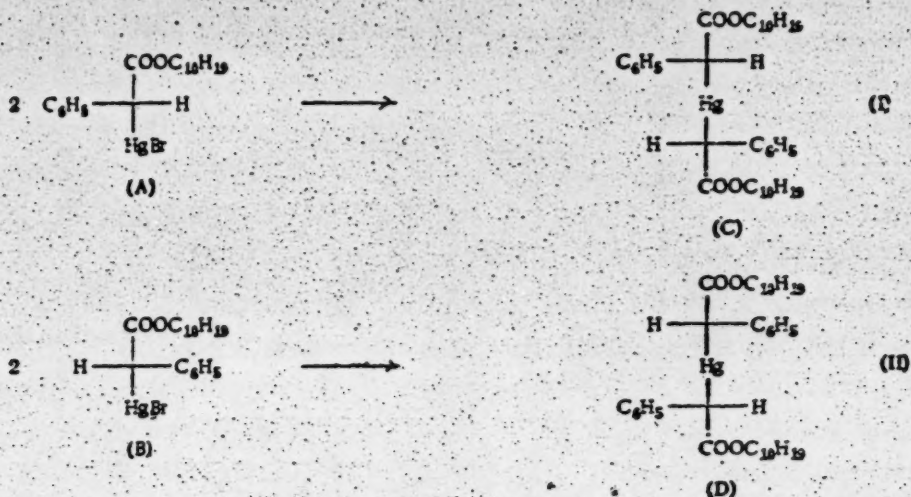HgBr

* The fact that the symmetrization reaction takes this course indicates that the free electron pair is able to fix the configuration of a carbon atom as in the case of sulfur [4].

** That the rupture of the bond $-\overset{}{\underset{}{C}} : HgBr$ will proceed in the way indicated in the scheme will be seen from the following considerations: rupture of the bond as indicated by $-\overset{}{\underset{}{C}} : HgBr$ is impossible since it is associ-
(−)
ated with formation of the anion HgBr, and if the bond C — Hg were ruptured homolytically $-\overset{}{\underset{}{C}} HgBr$, then the free radical formed would take up a planar configuration, which would lead to the formation of two diastereo-isomeric symmetrical organomercury compounds, instead of only one.

*** It can scarcely be doubted that reactions of this type, in which not only mercuric halide, but also highly dissociated mercury salts can take part [5], are electrophilic-substitution reactions.

The formation of the symmetrical organomercury compounds occurs, as has been shown above, with preservation of the configuration of the asymmetrical carbon atoms in both molecules of the original organomercury salt:

$$2 \quad C_6H_5 - \overset{\displaystyle COOC_{10}H_{19}}{\underset{\displaystyle HgBr}{|}} - H \quad \longrightarrow$$

(A)

$$C_6H_5 - \overset{\displaystyle COOC_{10}H_{19}}{|} - H \quad (\text{C})$$
$$Hg$$
$$H - \overset{|}{\underset{\displaystyle COOC_{10}H_{19}}{|}} - C_6H_5$$

(C)

$$2 \quad H - \overset{\displaystyle COOC_{10}H_{19}}{\underset{\displaystyle HgBr}{|}} - C_6H_5 \quad \longrightarrow$$

(B)

$$H - \overset{\displaystyle COOC_{10}H_{19}}{|} - C_6H_5 \quad (\text{D})$$
$$Hg$$
$$C_6H_5 - \overset{|}{\underset{\displaystyle COOC_{10}H_{19}}{|}} - H$$

(D)

The reactions of the symmetrical organomercury compounds C and D with mercuric bromide may theoretically proceed in the following ways:

1. The configurations of both asymmetrical carbon atoms may be preserved. In that case the menthyl ester of (bromomercuri)phenylacetic acid obtained will be the diastereoisomer from which the given symmetrical organomercury compound was prepared (by symmetrization with ammonia). For example, in this case the symmetrical compound having $[a]_D^{18} -21.4°$, which was prepared by the symmetrization of $C_6H_5-\underset{HgBr}{CH}-COOC_{10}H_{19}$, for which $[a]_D^{18}$ is $-96.5°$, will react with mercuric bromide to give $C_6H_5-\underset{HgBr}{CH}-COOC_{10}H_{19}$, for which $[r]_D^{18}$ is again $-96.5°$; and the symmetrical compound having $[a]_D^{18} -7.7°$ (obtained from $C_6H_5-\underset{HgBr}{CH}-COOC_{10}H_{19}$ having $[a]_D^{18} -49.3°$) will react with mercuric bromide to give the organomercury salt having $[a]_D^{18} -49.3°$.

2. The configuration of one carbon atom may be preserved, and that of the other may be inverted. In that case both of the symmetrical organomercury compounds, C and D, should give the same product by reaction with mercuric bromide: an equimolecular mixture of diastereoisomers.

3. The reaction of the symmetrical compounds with mercuric bromide may be accompanied by preservation of the configuration of one carbon atom and racemization of the other half of the molecule*. In that case reaction of the symmetrical organomercury compound having $[a]_D^{18} -21.4°$, with mercuric bromide should give a mixture of diastereoisomers of $C_6H_5-\underset{HgBr}{CH}-COOC_{10}H_{19}$, consisting of 75% of the compound having $[a]_D^{18} -96.5°$ and 25% of the compound having $[a]_D^{18} -49.3°$; and reaction of the symmetrical compound having $[a]_D^{18} -7.7°$ with mercuric bromide should give a mixture of diastereoisomers of $C_6H_5-\underset{HgBr}{CH}-COOC_{10}H_{19}$ consisting of 75% of the compound having $[a]_D^{18} -49.3°$ and 25% of the compound having $[a]_D^{18} -96.5°$.

Actually, reaction of mercuric bromide both with the symmetrical compound having $[a]_D^{18} -21.4°$ and with the symmetrical compound having $[a]_D^{18} -7.7°$ yields an equimolecular mixture of diastereoisomers of $C_6H_5-\underset{HgBr}{CH}-COOC_{10}H_{19}$, which constitutes a proof that the reaction proceeds according to the second variant.

* As it is obvious that reaction with mercuric bromide is concerned with only one of two asymmetrical carbon atoms, we have not considered the following clearly improbable variants: 1) inversion of the configurations of both halves of the molecules; 2) inversion of the configuration of one half of the molecule and racemization of the other half; 3) racemization of both halves of the molecule.

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Before this inference concerning the mechanism of the electrophilic substitution of the symmetrical organo-mercury compound may be regarded as reliable, it is necessary to remove one fundamental difficulty. Since the reaction investigated is brought about by the boiling of an acetone solution of equimolecular amounts of the symmetrical organomercury compound and mercuric bromide for six hours, it is necessary to consider the possibility of a secondary "racemization" of the unsymmetrical organomercury diastereoisomers formed. Such "racemization" might be expected to occur when either of the diastereoisomers of C_6H_5—CH—$COOC_{10}H_{19}$ is boiled in acetone solu-

HgBr

tion with mercuric bromide; the latter is present in the reaction mixture together with symmetrical and unsymmetrical organomercury compounds, for the reaction does not occur instantaneously, but over a fairly long period of time. In absence of mercuric bromide, no "racemization" occurs in boiling alcoholic or acetone solutions of the symmetrical and unsymmetrical diastereoisomers, as the possibility of separating the diastereoisomers by fractional crystallization shows.

A special investigation showed that, whereas the unsymmetrical diastereoisomer having $[\alpha]_D^{\text{23}}$ −95°, for example, fully retained its rotation after being boiled for eight hours in acetone solution, a six-hour boil of the acetone solution with mercuric bromide led to partial "racemization" •. The rotatory power became $[\alpha]_D^{\text{19}}$ −80.2° (the rotatory power of the equimolecular mixture of diastereoisomers was $[\alpha]_D^{\text{23}}$ −73°). Hence, the reaction of $HgBr_2$ with C_6H_5—CH—$COOC_{10}H_{19}$ is slow. This gave us reason to hope that in a mixture of symmetrical organomercury com-

HgBr

pounds, unsymmetrical organomercury compound, and mercuric bromides, the latter would react with the symmetrical compound without effecting C_6H_5—CH—$COOC_{10}H_{19}$.

HgBr

A special experiment confirmed this supposition. In an eight-hour boil of an acetone solution of equimolecular amounts of mercuric bromide and the symmetrical organomercury compound together with twice the amount of the pure diastereoisomer of C_6H_5—CH—$COOC_{10}H_{19}$ having $[\alpha]_D^{\text{19}}$ −56°, the mercuric bromide reacted only with the sym-

HgBr

metrical compound, without affecting the unsymmetrical compound. On the basis of these experiments it may be definitely asserted that in the course of the reaction of di-(−)-menthyl esters of mercuribis[phenylacetic acid] with mercuric bromide there is no "racemization" of the unsymmetrical diastereoisomers.

The formation of an equimolecular mixture of unsymmetrical diastereoisomers A and B by the reaction of the symmetrical diastereoisomers C and D with mercuric bromide proves, therefore, that these electrophilic-substitution reactions at a saturated carbon atom are accompanied by inversion of the configuration at this carbon atom:
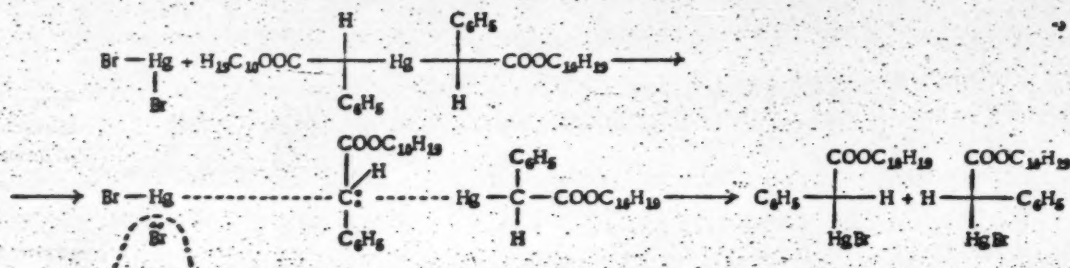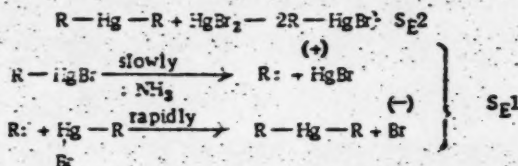

• On the basis of this fact we may already advance the hypothesis that the electrophilic substitution of an isomer of the unsymmetrical organomercury compound by mercuric bromide proceeds with inversion of configuration:
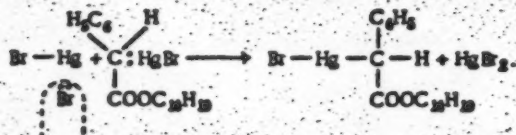
Hence, the electrophilic substitution reaction of mercuric chloride with di-(−)-menthyl esters of mercuribis-[phenylacetic acid] is accompanied by inversion of the configuration of the asymmetrical carbon atom, and the reaction of symmetrization of menthyl esters of (···mercuri)phenylacetic acid are also electrophilic substitution reactions, occurring with preservation of configuration. These circumstances can be understood if it is supposed that the mechanism of electrophilic substitution at a saturated carbon atom can vary according to the nature of the hydrocarbon radical at the atom (or group of atoms) being substituted and to the nature of the solvent, as is true of nucleophilic substitution. In that case, an electrophilic substitution reaction proceeding with preservation of configuration must correspond to nucleophilic substitution reactions proceeding by mechanism S_N1 (more accurately, by the "carbonium mechanism" [2]), and an electrophilic substitution reaction proceeding with inversion of configuration must correspond to nucleophilic substitution reactions proceeding by mechanism S_N2 (more accurately, by the "mechanism of direct substitution" [2]).

Whereas S_N1 nucleophilic substitution reactions, e.g. the hydrolysis of alkyl halides, go readily in a medium of polar electrophilic substances, e.g. in formic acid, S_E1 electrophilic substitution reactions of organomercury (and other organometallic) compounds should be facilitated by the presence of polar nucleophilic substances, such as ammonia, and this was found to be true in one of the cases that we investigated.

The difference in the stereochemical courses of the electrophilic substitution reactions that we investigated is therefore to be explained, in our opinion, by difference in mechanism:

$$R-Hg-R + HgBr_2 \longrightarrow 2R-HgBr \quad S_E2$$

$$\left.\begin{array}{l} R-HgBr \xrightarrow[: NH_3]{slowly} R: + HgBr \quad (+) \\[1em] R: + Hg-R \xrightarrow{rapidly} R-Hg-R + Br \quad (-) \\ \quad\quad Br \end{array}\right\} \quad S_E1$$

This hypothesis, of course, requires verification with the aid of kinetic methods of investigation.

EXPERIMENTAL

1. Symmetrization of the Isomer of the (−)-Menthyl Ester of (Bromomercuri)phenyl-acetic Acid having $[\alpha]_D^{18} - 95°$

Dry ammonia was passed for two hours through a solution of 10 g of the (−)-menthyl ester of (bromomercuri)-phenylacetic acid having m.p. 161-162° and $[\alpha]_D^{18} - 95°$ in 150 ml of dry chloroform. The precipitate of chloro-amidomercury was filtered off. The filtrate still contained some non-symmetrized organomercury compound, and was therefore again saturated with ammonia and left overnight. The further amount of chloroamidomercury that formed was filtered off (total amount 3.2 g), and the chloroform was evaporated off. The oil that remained solidi-fied after one day, and 7 g (quantitative yield) of non-recrystallized product was obtained. After crystallization from methanol it melted at 112-115° and had $[\alpha]_D^{18} = 14.1°$ (C = 3.44; l = 2; $\alpha_D -0.87°$). The substance was recrystallized further from ethanol. The first recrystallization gave m.p. 118-122°, $[\alpha]_D^{18} - 17.5°$ (C = 4.05; l = 2; $\alpha_D -1.25°$). The second recrystallization gave m.p. 119-122° $[\alpha]_D^{18} - 21°$ (C = 4.06; l = 2; $\alpha_D = 1.33°$). In further recrystallizations the rotatory power and melting point of the substance remained the same; after the third recrystallization they were m.p. 119-122°; $[\alpha]_D^{18} - 21.4°$ (C = 3.32, l = 2; $\alpha_D -1.25°$).

Found %: C 57.89; 57.65; H 6.63; 6.51
$C_{18}H_{25}O_2Hg$.   Calculated %: C 57.83;   H 6.77

The substance is described for the first time.

The filtrate from the first recrystallization did not contain any other isomer of the symmetrical organomercury compound; only the same isomer, somewhat contaminated and in small amount, m.p. 119-122° and $[\alpha]_D^{18} - 21.4°$, could be isolated from it. Hence as a result of the isomerization of the isomer of the (−)-menthyl ester of (bromo-mercuri)phenylacetic acid having $[\alpha]_D^{18} - 95°$, one single isomer is formed of the di-(−)-menthyl ester of mercuri-bis[phenylacetic acid], $[\alpha]_D^{18} - 21.4°$ and m.p. 119-122°.

2. Symmetrization of the Isomer of the (−)-Menthyl Ester of (Bromomercuri)phenyl-acetic Acid having $[\alpha]_D^{18} - 49.3°$

Under the conditions of the preceding experiment, 7 g of the (−)-menthyl ester of (bromomercuri)phenylacetic

acid having m.p. 152-154° and $[a]_D^8 -49.3°$ yielded 4.5 g of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] (93.8% yield). Recrystallization from methanol yielded 2.7 g of a substance of m.p. 118-120° and $[a]_D^{18} -8.1 \pm 0.15°$ (C = 3.38; l = 2; $a_D -0.48°$). Further recrystallizations did not affect the rotatory power and melting point; for example, after the second recrystallization they were m.p. 118-120°; $[a]_D^{18} -7.7° \pm 0.3°$ (C = 3.87; l = 2; $a_D -0.52°$).

$$\text{Found \%: C 57.98; 57.90; H 6.83; 6.70}$$

$C_{36}H_{56}O_4Hg.$ Calculated %: C 57.85;   H 6.74

The substance is described for the first time.

3. Preservation of the Configuration of the (−)-Menthyl Ester of (Bromomercuri)phenylacetic Acid during Boiling in Acetone Solution

A solution of 0.7 g of the pure isomer of the (−)-menthyl ester of (bromomercuri)phenylacetic acid having m.p. 161.5-162.5° and $[a]_D^{18} -95°$ in 50 ml of dry acetone was heated at the boil for eight hours. The acetone was evaporated off, and the remaining substance was crystallized from methanol, yielding a substance of m.p. 160-162° and $[a]_D^{18} -94.4°$ (C = 0.754; l = 2; $a_D -1.25°$). The configuration of the molecules of the substance was therefore completely preserved under these conditions.

4. "Racemization of the (−)-Menthyl Ester of (Bromomercuri)phenylacetic Acid under the Action of Mercuric Bromide in Acetone

An acetone solution of 0.5 g (0.0009 mole) of the (−)-menthyl ester of (bromomercuri)phenylacetic acid (m.p. 158-159° and $[a]_D^{18} -90.3°$) and 0.35 g (0.001 mole) of mercuric bromide were heated at the boil for six hours. The acetone was evaporated off, and the residual substance was treated with chloroform, the undissolved mercuric bromide being filtered off. The substance that remained after evaporation of chloroform was recrystallized from methanol; m.p. 154-155°; $[a]_D^{18} -80.2°$ (C = 0.74; l = 2; $a_D -1.04°$).

Under the action of mercuric bromide, therefore, slow "racemization" of the (−)-menthyl ester of (bromomercuri)phenylacetic acid occurs (the rotatory power of an equimolecular mixture of diastereoisomers is −73°).

5. Reaction of Mercuric Bromide with the Di-(−)-menthyl Ester of Mercuribis[phenylacetic acid] in Presence of the (−)-Menthyl Ester of (Bromomercuri)phenylacetic Acid

An acetone solution of a mixture of 0.75 g (0.001 mole) of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] (m.p. 116-118°; $[a]_D^{B} -5.5°$), 1.1 g (0.002 mole) of the menthyl ester of (bromomercuri)phenylacetic acid (m.p. 161-162°; $[a]_D^{18} -96°$), and 0.36 g (0.001 mole) of mercuric bromide was heated at the boil for eight hours. The acetone was evaporated off, and the residual substance was crystallized from carbon tetrachloride, yielding a substance of m.p. 157-158° and $[a]_D^{B} -85.9° \pm 1°$ (C = 0.781; l = 2; $a_D -1.18°$).

Reaction of mercuric bromide with 0.75 g of the symmetrical compound yields 1.1 g of an equimolecular mixture of the (−)-menthyl esters of (+)- and (−)-(bromomercuri)phenylacetic acids having $[a]_D^{B} -73°$. If we suppose that the mercuric bromide did not "racemize" the 1.1 g of the menthyl ester of (bromomercuri)phenylacetic acid having $[a]_D^{B} -96°$ that was added to the reaction mixture, the rotatory power of the product would be expected to be $\frac{-73° -96°}{2} = -84.5°$. As will be seen, this value is practically the same as the rotatory power of the substance formed in the reaction. Mercuric bromide, therefore, reacts with the symmetrical compound without affecting the unsymmetrical one, the configuration of which is preserved.

6. Reaction of Mercuric Bromide with the Diastereoisomers of the Di-(−)-menthyl Ester of Mercuribis[phenylacetic acid]

a) A mixture of 0.9 g (0.0012 mole) of the di-(−)-menthyl ester of mercuribis[phenylacetic acid] (m.p. 119-122°; $[a]_D^{18} -21.4°$) and 0.43 g (0.0012 mole) of mercuric bromide was heated in acetone solution at the boil for six hours. Completion of reaction was established by testing (with alkali) for the disappearance of mercuric chloride from the reaction mixture. The acetone was distilled off, and the residue was crystallized from carbon tetrachloride, yielding a substance of m.p. 155-157° and $[a]_D^{B} -72.6°$ (C = 0.784; l = 2; $a_D -1.00°$). A mixture test with known (−)-menthyl ester of (bromomercuri)phenylacetic acid (m.p. 157-158°) gave no depression of melting point (mixture melted at 156-157°). Hence, as a result of the reaction an equimolecular mixture of diastereoisomerci menthyl esters of (bromomercuri)phenylacetic acid was formed.

b) A mixture of 0.95 g (0.0013 mole) of the di-(–)-menthyl ester of mercuribis[phenylacetic acid] (m. p. 115-120°; $[a]_D^{18} - 7.7°$) and 0.46 g (0.0013 mole) of mercuric bromide was heated in acetone solution at the boil for six hours. Completion of reaction was determined as in the preceding experiment. The acetone was distilled off, and the residue was crystallized from carbon tetrachloride, yielding a substance of m.p. 157-158° and $[a]_D^{18} - 72.5°$ ($C = 0.69; 1 = 2, a_D - 0.87$). A mixture test with known (–)-menthyl ester of (bromomercuri)phenylacetic acid (m.p. 157-158°) gave no depression of melting point (mixture melted at 157-158°). Hence, as a result of the reaction an equimolecular mixture of diastereoisomeric menthyl esters of (bromomercuri)phenylacetic acid was formed.

SUMMARY

1. Two diastereoisomers of the di-(–)-menthyl ester of mercuribis[phenylacetic acid] have been prepared in the pure state.

2. The mechanism of the symmetrization of organomercury compounds of the aliphatic series under the action of nucleophilic reagents has been elucidated.

3. The stereochemical course of an electrophilic-substitution reaction at a saturated carbon atom has been investigated for the first time, the examples studied being the symmetrization of diastereoisomeric menthyl esters of (bromomercuri)phenylacetic acid and the reaction of the diastereoisomeric di-(–)-menthyl esters of mercuribis[phenylacetic acid] with mercuric bromide. It has been shown that the electrophilic-substitution reaction proceeds with retention of the configuration at the asymmetric carbon atom in the first case, and with inversion of the configuration in the second case.

4. A hypothesis has been advanced concerning the causes of the different stereochemical courses of the electrophilic-substitution reactions in the cases investigated.

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GRIGNARD SYNTHESIS OF TETRAPHENYLSILANE, TETRA-p-TOLYLSILANE,

AND FLUOROTRI-p-TOLYLSILANE

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It is known from the literature [1-3] that the synthesis of tetraarylsilanes that do not exhibit high steric-hindrance effects, such as tetraphenylsilane and tetra-p-tolylsilane, by the Grignard method may be effected only at elevated temperatures obtained by replacement of ether by a higher-boiling solvent. Under the usual conditions of synthesis, however, even when a large excess of arylmagnesium halide is boiled for a long time in an ether medium with tetrachlorosilane [4] or tetraethoxysilane [3], the reaction stops when the corresponding tri-arylhalo- or triarylethoxy-silane is formed. Our investigations have shown, however, that tetraphenyl- and tetra-p-tolyl-silanes can be obtained in good yields under the conditions of the Grignard synthesis when silicon tetra-fluoride and excess of arylmagnesium halide are used as starting materials. When, for example, a mixture of sili-con tetrafluoride and a two-fold excess of phenylmagnesium bromide was heated in a water bath, we obtained tetraphenylsilane in about 30% yield, about 14% of fluorotriphenylsilane [5] being obtained at the same time. Under the same conditions tetra-p-tolylsilane [6] was obtained in about 22% yield, and about 10% of fluorotri-p-tolylsilane, m.p. 103-104°, was obtained at the same time. If however, stoichiometric amounts of the reactants are used (1 mole of SiF$_4$ to 4 moles of p-tolylmagnesium bromide), then only fluorotri-p-tolylsilane is formed, even after prolonged boiling (as in the case of the synthesis of fluorotriphenylsilane).

EXPERIMENTAL

1. Tetraphenylsilane. Silicon tetrafluoride, obtained by dropping 300 ml of concentrated sulfuric acid into a mixture of 25 g of sodium fluosilicate and 15 g of finely-ground glass, was passed over a period of five hours into a constantly stirred solution of phenylmagnesium bromide prepared by dissolving 24 g of magnesium in a mixture of 500 ml of absolute ether and 157 g of bromobenzene. The ether was driven off, and the mixture was boiled in a water bath for four hours. The complex, cooled with ice water, was decomposed with 30% acetic acid, ether being added also. Ether-insoluble tetraphenylsilane separated, and was filtered off. Two crystallizations from toluene yielded 11.5 g (30% on the silicon tetrafluoride) of finely crystalline tetraphenylsilane, which we identified by its melting point (233-234°).

Fractionation of the ether extract yielded a fraction of b.p. 245-252°/30 mm, and from this, after crystal-lization from ether, we isolated 5.3 g of fluorotriphenylsilane in the form of large clear prisms, m.p. 63-64°, which is in accord with data in the literature [5].

2. Tetra-p-tolylsilane. Silicon tetrafluoride, obtained from 12.5 g of sodium fluosilicate, 150 ml of sulfuric acid, and 8 g of glass powder, was passed over a period of three hours into a solution of 0.5 mole of p-tolylmag-nesium bromide prepared from 12 g of magnesium, 450 ml of ether, and 85 g of p-bromotoluene. Ether was removed, and the mixture was boiled in a water bath for five hours. The complex was cooled and decomposed as described above, and the tetra-p-tolylsilane that separated from ether solution was recrystallized from toluene, yielding 5 g (22%) of finely crystalline tetra-p-tolylsilane, m.p. 223-227°.

When the ether extract was fractionated, two fractions were collected. Fraction I, b.p. 205-214°/35 mm, was crystallized from ether, and 0.8 g of the by-product p,p'-bitolyl, m.p. 121°, was isolated. Fraction II (5.4 g; b.p. 245-252°/35mm) yielded 2.1 g (10% on the SiF$_4$ taken) of fluorotri-p-tolylsilane, m.p. 103-104°. Fluorotri-p-tolyl-silane, like fluorotriphenylsilane, crystallizes from ether in the form of large clear prisms. Under atmospheric con-ditions it boils at 324-327° without decomposition. It is of good solubility in benzene, toluene, chloroform, and

carbon tetrachloride.

$$\begin{aligned} &\text{Found \%:} && \text{Si } 8.5; \ 8.1 \\ \text{C}_{21}\text{H}_{21}\text{SiF.} \quad &\text{Calculated \%:} && \text{Si } 8.7 \\ &\text{Found \%:} && \text{F } 6.0; \ 6.2; \ \text{M } 323; \ 334 \\ \text{C}_{21}\text{H}_{21}\text{SiF.} \quad &\text{Calculated \%:} && \text{F } 5.9; \quad \ \ \text{M } 324 \end{aligned}$$

3. Fluorotri-p-tolylsilane. Silicon tetrafluoride, obtained from 25 g of sodium fluosilicate, 300 ml of concentrated sulfuric acid, and 15 g of glass powder, was passed over a period of five hours into an ethereal solution of p-tolylmagnesium bromide prepared from 12 g of magnesium and 85 g of p-bromotoluene. The ether was removed, and the mixture was boiled in a water bath for five hours. The complex was cooled and decomposed with 30% acetic acid. Under these conditions the separation of ether-insoluble tetra-p-tolylsilane was not observed. Fractionation of the ether extract yielded 24.6 g of a fraction of b.p. 246-252°/25 mm, and recrystallization of this from ether yielded 17.5 g (42% on the SiF$_4$ taken) of fluorotri-p-tolylsilane, the properties of which are given above.

SUMMARY

1. It has been established that, when silicon tetrafluoride reacts with a two-fold excess of phenyl- or p-tolyl-magnesium bromide under the conditions of the Grignard synthesis, the corresponding tetraarylsilane is obtained in good yield.

2. Fluorotri-p-tolylsilane has been synthesized for the first time, and some of its properties have been determined.

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REACTIONS OF ALDEHYDES WITH PHOSPHONOUS AND PHOSPHINOUS CHLORIDES

M. I. Kabachnik and E. S. Shepeleva

In previous papers we have shown [1] that, when an aldehyde is heated with phosphorus trichloride in a sealed tube or autoclave at 160-250°, an α-chloro phosphonic dichloride is obtained:

$$RCHO + PCl_3 = RCHCl - POCl_2.$$
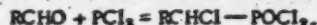
If instead of phosphorus trichloride a diaryl phosphorochloridite is used, it is possible to obtain a diaryl 1-chloro-alkylphosphonate in satisfactory yield [2]:

$$RCHO + Cl - P\begin{matrix} OAr \\ \\ OAr \end{matrix} = RCHCl - PO(OAr)_2.$$
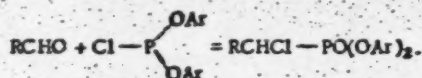
It was of interest to determine the extent to which our reaction was applicable to phosphonous and phosphinous chlorides, i.e., to substances already having a C — P bond in the molecule. If phosphonous dichlorides react like phosphorus trichloride, then α-chloro phosphinic chlorides should be formed. For example, from alkyl-phosphonous dichlorides and aldehydes, alkyl-1-chloroalkylphosphinic chlorides should be obtained:

$$RCHO + R'PCl_2 = \begin{matrix} RClCH & O \\ & P \\ R' & Cl \end{matrix}$$
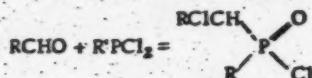
In a similar way, from diarylphosphinous chlorides, diaryl-1-chloroalkylphosphine oxides should be obtained:

$$RCHO + Ar_2PCl = RClCH - \begin{matrix} O \\ P \\ Ar \\ Ar \end{matrix}$$
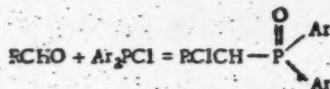
These conclusions were found to be correct. We investigated the reactions of paraformaldehyde with the most accessible phosphonous dichlorides, ethyl- [3] and phenyl-phosphonous dichlorides [4]. Ethylphosphonous dichloride and paraformaldehyde reacted when heated in a sealed tube at 200° for 2 hours 30 minutes, and gave a 30% yield of (chloromethyl)ethylphosphinic chloride (I). This substance has all of the properties of an acid chloride; thus, when it is poured into ethanol, the chlorine atom is smoothly replaced by an ethoxyl group, and ethyl (chloromethyl)ethylphosphinate (II) is formed.

The reaction of phenylphosphonous dichloride with paraformaldehyde requires more severe conditions: the tubes containing the mixture of reactants must be heated to 230-250°. (Chloromethyl)phenylphosphinic chloride (III) was obtained in 47% yield. When it was poured into cooled absolute methanol or ethanol, the corresponding esters (V and VI) were obtained; they are colorless glycerollike liquids, readily soluble in water and organic solvents. Hydrolysis of (chloromethyl)phenylphosphinic chloride was accompanied by some evolution of heat, and crystalline (chloromethyl)phenylphosphinic acid (IV) was obtained.

Diphenylphosphinous chloride reacted with paraformaldehyde when heated in a sealed tube at 240-250° for two hours, and a high-boiling substance, (chloromethyl)diphenylphosphine oxide, was obtained in 40% yield. The constants of the substances obtained are given in the table.

We consider that the mechanism of the formation of phosphinic chlorides from paraformaldehyde and phosphonous dichlorides is quite similar to the mechanism of the reaction of phosphorous trichloride with aldehydes, which we have examined previously [1]. That is to say, in the first stage, which occurs already in the cold, two

No.	Formula	B.p. in °C (pressure in mm Hg)	M.p. (°C)	d_4^{20}	n_D^{20}	MR_D Found	Calculated*
(I)	C_2H_5 — P(=O)(ClCH$_2$)(Cl)	83–84 (3.5)	—	1.3628	1.4937	34.35	34.32
(II)	C_2H_5 — P(=O)(ClCH$_2$)(OC$_2$H$_5$)	78–78.5 (3)	—	1.1632	1.4570	39.92	39.96
(III)	C_6H_5 — P(=O)(ClCH$_2$)(Cl)	116–117 (2)	47–49	—	—	—	—
(IV)	C_6H_5 — P(=O)(ClCH$_2$)(OH)	—	93–93.5	—	—	—	—
(V)	C_6H_5 — P(=O)(ClCH$_2$)(OCH$_3$)	125–126 (2.5)	—	1.2654	1.5409	50.76	50.21
(VI)	C_6H_5 — P(=O)(ClCH$_2$)(OC$_2$H$_5$)	132–134 (2.5)	—	1.2329	1.5275	54.53	54.83
(VII)	C_6H_5 — P(=O)(C$_6$H$_5$)(CH$_2$Cl)	146–147 (2)	122–124	—	—	—	—

molecules of the aldehyde add to the phosphonous dichloride with formation of a bis(chloroalkyl) ester of a phosphonous acid:
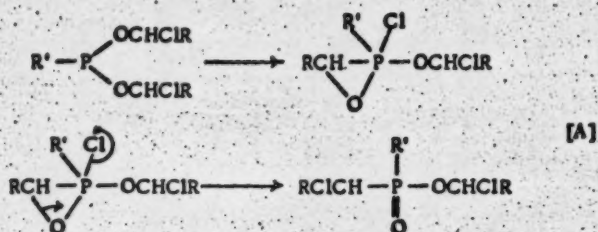
$$2RCHO + R'PCl_2 = R'P(OCHClR)(OCHClR)$$
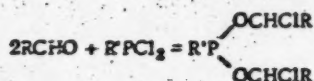
This substance should be extremely prone to undergo the Arbuzov rearrangement, which will occur under the influence of the alkyl-halide function contained in the ester grouping, no addition of alkyl halide being necessary: on the one hand, Arbuzov and Rizpolozhensky [5] have recently shown that ethylphosphonous esters readily undergo the Arbuzov rearrangement, and the readiness with which phenylphosphonous esters undergo the rearrangement has long been known from the work of A. E. Arbuzov [6]; and on the other hand, Abramov [7] has shown that α-chloro esters bring about the Arbuzov rearrangement of trialkyl phosphites already in the cold. There can be no doubt, therefore, that the bis(chloromethyl) (or similar) ester of ethyl- or phenyl-phosphonous acid, once formed, will quickly undergo Arbuzov rearrangement with formation of the chloromethyl (chloroalkyl) ester of a (chloromethyl)-ethylphosphinic acid [or (chloromethyl)phenylphosphinic acid]:
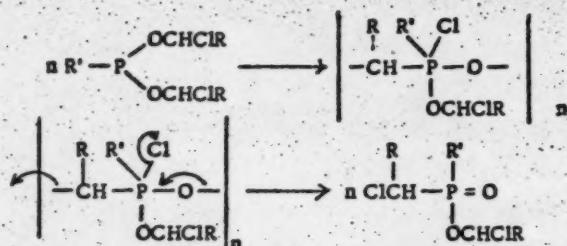
$$R' — P(OCHClR)(OCHClR) \rightarrow R'(RClCH)P(OCHClR)(=O)$$
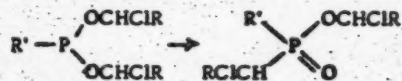
How the rearrangement will occur, intra- or inter-molecularly, cannot be predicted. In the first case the

*The atomic refraction of phosphorus in phosphinic acid derivatives is not known. We have deduced the value $AR_P = 4.85$ from a limited number of data, and it must therefore be regarded as a preliminary value.
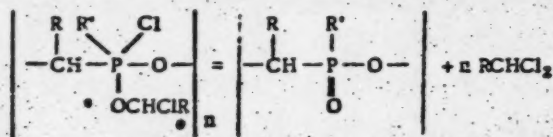
Intermediate phosphonium compound must be cyclic:

$$\text{R' — P}\begin{smallmatrix}\text{OCHClR}\\\text{OCHClR}\end{smallmatrix} \longrightarrow \overset{\text{R'}\quad\text{Cl}}{\text{RCH —}}\underset{\text{O}}{\text{P}}\text{— OCHClR}$$

$$\overset{\text{R'}\quad\text{Cl}}{\text{RCH —}}\underset{\text{O}}{\text{P}}\text{— OCHClR} \longrightarrow \overset{\text{R'}}{\text{RClCH —}}\underset{\text{O}}{\text{P}}\text{— OCHClR}$$

[A]

In the second case the intermediate phosphonium compound must have a polymeric character, since it is formed by the alkylation at the phosphorus atom of one molecule by the chloroalkyl group of another. If we represent only the repeating unit of the polymeric phosphonium compound, the intermolecular rearrangement can be represented as:

$$n\ \text{R' — P}\begin{smallmatrix}\text{OCHClR}\\\text{OCHClR}\end{smallmatrix} \longrightarrow \left|\overset{\text{R}\ \text{R'}\ \text{Cl}}{\underset{\text{OCHClR}}{\text{—CH—P—O—}}}\right|_n$$

$$\left|\overset{\text{R}\ \text{R'}\ \text{Cl}}{\underset{\text{OCHClR}}{\text{—CH—P—O—}}}\right|_n \longrightarrow n\ \overset{\text{R}}{\underset{\text{OCHClR}}{\text{ClCH—P=O}}}$$
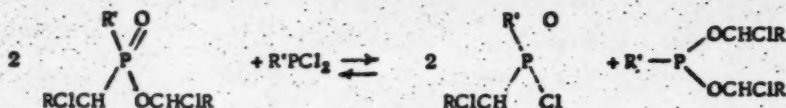
The formation (as in the case of the reaction of paraformaldehyde with phosphorus trichloride [1]) of a large amount of undistillable residue indicates that some intermolecular reaction undoubtedly occurs, for only then could a polymeric residue be formed; it is formed in the second stage of the Arbuzov rearrangement by the elimination of the chloroalkyl side groups without effect on the main chain:

$$\left|\overset{\text{R}\ \text{R'}\quad\text{Cl}}{\underset{\text{OCHClR}}{\text{—CH—P—O—}}}\right|_n = \left|\overset{\text{R}\quad\text{R'}}{\underset{\text{O}}{\text{—CH—P—O—}}}\right| + n\ \text{RCHCl}_2$$
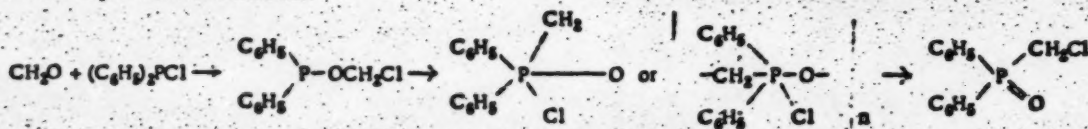
Whether there is simultaneous intramolecular alkylation in accordance with scheme A it is as yet impossible to say.

The last stage in the formation of an alkyl(chloroalkyl)phosphinic chloride is the metathetic reaction of the Arbuzov-rearrangement product with a second molecule of the phosphonous dichloride:

$$2\ \overset{\text{R'}\ \text{O}}{\underset{\text{RClCH}\quad\text{OCHClR}}{\text{P}}} + \text{R'PCl}_2 \rightleftarrows 2\ \overset{\text{R'}\ \text{O}}{\underset{\text{RClCH}\quad\text{Cl}}{\text{P}}} + \text{R' — P}\begin{smallmatrix}\text{OCHClR}\\\text{OCHClR}\end{smallmatrix}$$

The final reaction product, an alkyl-1-chloroalkylphosphinic chloride, and some fresh bis(chloroalkyl) ester of a phosphonous acid, R' — P(OCHClR)$_2$, are formed. The latter again undergoes the Arbuzov rearrangement, etc., until the whole of the phosphonous dichloride has reacted.

We give our proposed scheme for the mechanism of the reaction of diphenylphosphinous chloride with paraformaldehyde without comment:

$$\text{CH}_2\text{O} + (\text{C}_6\text{H}_5)_2\text{PCl} \rightarrow \overset{\text{C}_6\text{H}_5}{\underset{\text{C}_6\text{H}_5}{\text{P}}}\text{—OCH}_2\text{Cl} \rightarrow \overset{\text{C}_6\text{H}_5\quad\text{CH}_2}{\underset{\text{C}_6\text{H}_5\quad\text{Cl}}{\text{P}}}\text{—O}\ \text{or}\ \left|\overset{\text{C}_6\text{H}_5}{\underset{\text{C}_6\text{H}_5\quad\text{Cl}}{\text{—CH}_2\text{—P—O—}}}\right|_n \rightarrow \overset{\text{C}_6\text{H}_5\quad\text{CH}_2\text{Cl}}{\underset{\text{C}_6\text{H}_5\quad\text{O}}{\text{P}}}$$

EXPERIMENTAL

(Chloromethyl)ethylphosphinic Chloride (I). We prepared our ethylphosphonous dichloride by Michaelis's method [3]. Ethylphosphonous dichloride (13.1 g) and paraformaldehyde (3 g) were mixed with cooling, sealed in a tube, and heated at 200° for 2 hours 30 minutes. The light-yellow mobile liquid obtained was vacuum-fractionated, and after four successive fractionations 5.8 g (36%) of a fraction of b.p. 83-84°/3.5 mm was obtained.

(Chloromethyl)ethylphosphinic chloride is a colorless mobile liquid; n_D^{10} 1.4937; d_4^{20} 1.3625. Found MR_D 34.35; Calculated MR_D 34.32.

Found %: C 22.61; 22.70; H 4.28; 4.38; P 18.76; 19.17
$C_3H_7OPCl_2$. Calculated %: C 22.35; H 4.34; P 19.25

Ethyl (chloromethyl)ethylphosphinate (II). (Chloromethyl)ethylphosphinic chloride (2.6 g) was poured into cooled absolute ethanol (12 ml), and the mixture was set aside overnight. The excess of alcohol was distilled off, and the residue was vacuum-fractionated. Two fractionations yielded 1.5 g (72%) of a substance of b.p. 72-73.5°/3 mm.

Ethyl (chloromethyl)ethylphosphinate is a colorless liquid; d_4^{20} 1.1632; n_D^{20} 1.4570; Found MR_D 39.92; Calculated MR_D 39.96.

Found %: P 18.34
$C_5H_{12}O_2PCl$. Calculated %: P 18.19

(Chloromethyl)phenylphosphinic Chloride (III). We prepared our phenylphosphonous dichloride by Michaelis's method, as improved by Dye [4]. A mixture of 17.9 g of phenylphosphonous dichloride and 3 g of paraformaldehyde was heated in a sealed tube for two hours at 230-240°. The yellow mobile liquid formed was vacuum-fractionated, and yielded 9.9 g (47%) of a substance of b.p. 116-117°/2 mm, which rapidly solidified in the receiver.

(Chloromethyl)phenylphosphinic chloride forms white hygroscopic crystals, melting in a sealed capillary at 47-49°.

Found %: P 14.46; 14.51
$C_7H_7OPCl_2$. Calculated %: P 14.83

(Chloromethyl)phenylphosphinic Acid (IV). (Chloromethyl)phenylphosphinic chloride (2 g) was dissolved in water (15 ml); some heat was evolved, and hydrogen chloride was given off. Repeated evaporation with water yielded some crystals, and these were recrystallized from dry benzene with an addition of petroleum ether, and then again recrystallized from water. Yield 60%; m.p. 93-93.5°. The acid readily dissolves when warmed with absolute alcohol; it is difficultly soluble in benzene, petroleum ether, water, and ether.

Found %: C 44.13; 44.44; H 4.43; 4.44; P 16.10; 15.90
$C_7H_8O_2PCl$. Calculated %: C 44.09   H 4.20   P 16.28

Methyl (chloromethyl)phenylphosphinate (V). (Chloromethyl)phenylphosphinic chloride (3 g) was dissolved in cooled absolute ethanol (15 ml), and the mixture was set aside overnight. The excess of alcohol was distilled off, and the reaction mixture was vacuum-fractionated. Two fractionations yielded 1.4 g (47%) of a fraction boiling at 125-126° at 2.5 mm. This substance is a colorless liquid: n_D^{20} 1.5409; d_4^{20} 1.2654; Found MR_D 50.76. Calculated MR_D 50.21.

Found %: P 14.95; 14.82
$C_8H_{10}O_2PCl$. Calculated %: P 15.17

Ethyl (chloromethyl)phenylphosphinate (VI). (Chloromethyl)phenylphosphinic chloride (5 g) was dissolved in cooled absolute ethanol (20 ml) and set aside overnight. Two successive fractionations yielded 2 g (48%) of a substance of b.p. 132-133°/2.5 mm. This substance is a colorless liquid; n_D^{20} 1.5275; d_4^{20} 1.2329; Found MR_D 55.53; Calculated MR_D 54.83.

Found %: C 50.01; 50.00; H 5.66; 5.65
$C_9H_{12}O_2PCl$. Calculated %: C 49.43;   H 5.49

(Chloromethyl)diphenylphosphine Oxide (VII). We prepared our diphenylphosphinous chloride by the method of Meisenheimer and coworkers [8]. A mixture of 2.2 g of diphenylphosphinous chloride and 0.3 g of paraformaldehyde was heated in a sealed tube for two hours at 230-240°. Two fractionations yielded 0.8 g (40%) of a substance of b.p. 146-147°/2 m.n. which crystallized when cooled to below its melting point. The substance forms white hygroscopic crystals, which melt at 122-124° to a turbid liquid that clears at 135-137°.

<div align="center">
Found %: P 12.30; 11.97
$C_{13}H_{12}OPCl$. Calculated %: P 12.37
</div>

SUMMARY

1. It has been shown that paraformaldehyde reacts with alkyl- and aryl-phosphonous dichlorides with formation of alkyl- and aryl-(chloromethyl)phosphinic chlorides; the free phosphinic acids and their esters have been prepared.

2. It has been shown that diphenylphosphinous chloride reacts with paraformaldehyde with formation of (chloromethyl)diphenylphosphine oxide.

3. It has been suggested that the mechanism of the reaction of phosphonous and phosphinous chlorides with aldehydes is similar to that of the reaction of phosphorus trichloride with aldehydes and includes the stages of the formation of a bis(1-chloroalkyl)phosphonous ester, its Arbuzov rearrangement, and the replacement of ester groupings by chlorine.

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[2] M. I. Kabachnik and E. S. Shepeleva, Proc. Acad. Sci. USSR, 75, No. 2, 219 (1950).

[3] A. Michaelis, Ber. 13, 2174 (1880).

[4] A. Michaelis, Ann. 181, 265 (1876); W. T. Dye, J. Am. Chem. Soc. 70, 2595 (1948).

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[6] A. E. Arbuzov, J. Gen. Chem., 4, 898 (1934).

[7] V. S. Abramov, E. V. Sergeeva, and L. V. Chelpanova, J. Gen. Chem., 14, 1030 (1944).

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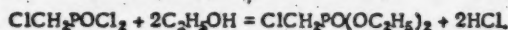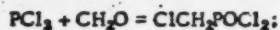# NEW METHOD FOR THE SYNTHESIS OF 1-AMINOALKYLPHOSPHONIC ACIDS

COMMUNICATION 1

M. I. Kabachnik and T. Ya. Medved

Until recently 1-aminoalkylphosphonic acids were difficultly accessible substances. The authors of this paper prepared the first member of this class of compounds, aminomethylphosphonic acid, from diethyl chloromethylphosphonate by heating it with 25% aqueous ammonia in a sealed tube at 150° for two hours [1]:

$$ClCH_2PO(OC_2H_5)_2 + 3NH_3 + H_2O = NH_2CH_2PO(OC_2H_5)ONH_4 + NH_4Cl + C_2H_5OH$$
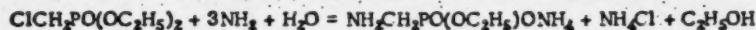
and then hydrolyzing the partial ester formed. The required ester of chloromethylphosphonic acid is readily synthesized in two stages from paraformaldehyde and phosphorus trichloride (first stage), and then alcohol (second stage), a method that was developed in our laboratory by Kabachnik and Shepeleva [2]:

$$PCl_3 + CH_2O = ClCH_2POCl_2;$$

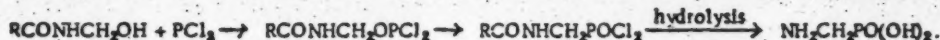$$ClCH_2POCl_2 + 2C_2H_5OH = ClCH_2PO(OC_2H_5)_2 + 2HCL$$

The whole synthesis of aminomethylphosphonic acid was therefore effected in three stages.

A few other cases of the synthesis of aminoalkylphosphonic acids have been described. Aminomethylphosphonic acid, for example, has been prepared from N-bromomethylphthalimide and sodium dibutyl phosphite, with subsequent hydrolysis of the phthalimide derivative with hydrobromic acid [3]:
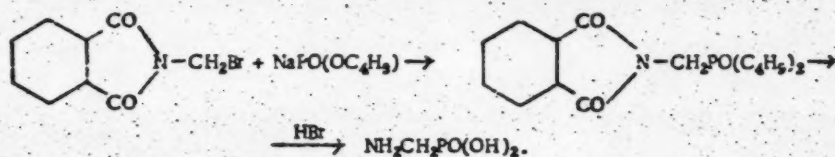
Also, according to patent literature, aminomethylphosphonic acid may be prepared from hydroxymethyl derivatives of amides and phosphorus trichloride; the acid chloride of the acylated amino acid that is first formed is subjected to complete hydrolysis [4]:

$$RCONHCH_2OH + PCl_3 \longrightarrow RCONHCH_2OPCl_2 \longrightarrow RCONHCH_2POCl_2 \xrightarrow{hydrolysis} NH_2CH_2PO(OH)_2.$$

Kosolapoff [5] synthesized α-aminobenzylphosphonic acid by the use of the p-nitrophenylhydrazone of diethyl benzoylphosphonate, which he prepared by Kabachnik and Rossyskaya's method [6]; for this, deep-seated reduction of the p-nitrophenylhydrazone was necessary:

$$C_6H_5COCl + P(OC_2H_5)_3 \longrightarrow C_6H_5COPO(OC_2H_5)_2 \longrightarrow$$
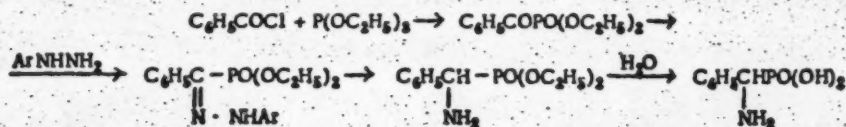
He also prepared 1-amino-1-phenylethylphosphonic acid from 1-chloro-1-phenylethylphosphonic acid [7].

Our method, cited above, of preparing aminomethylphosphonic acid from diethyl chloromethylphosphonate, although undoubtedly simpler than the other methods indicated, demands much labor and time, particularly in the separation of the reaction products from the reaction mixture. None of the described syntheses of amino

phosphonic acids is generally applicable, and all of them are multistage processes, so that amino phosphonic acids remain difficultly accessible.

It is, however, desirable to develop a direct and simple synthesis of compounds of this class. It is sufficient to point out that α-amino phosphonic acids are phosphorus analogs of α-amino carboxylic acids, the biological significance of which is enormous. The study of the properties of α-amino phosphonic acids is however greatly hindered by the absence of a good general method of synthesis.

Last year we reported that we had found a new method for the synthesis of esters of α-amino phosphonic acids in one stage by a reaction between an aldehyde, a dialkyl hydrogen phosphite, and ammonia [8]:

$$RCHO + HPO(OC_2H_5)_2 + NH_3 = RCH - PO(OC_2H_5)_2 + H_2O.$$
$$|$$
$$NH_2$$
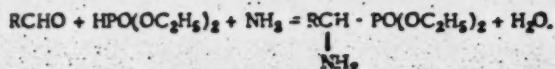
In the examples investigated we used benzaldehyde and piperonal, and diethyl and dibutyl hydrogen phosphites.

Later, a communication from Fields [9] appeared concerning the preparation of esters of α-amino phosphonic acids by the action of amines (primary and secondary) and aldehydes on dialkyl hydrogen phosphites. The author states that the reaction is applicable only to the synthesis of esters of aminoalkylphosphonic acids that are substituted at the nitrogen (Fields did not prepare the free amino phosphonic acids). We, however, have found that the synthesis of unsubstituted amino phosphonic acids—the most interesting compounds of this class, as will be shown in this paper—can be effected with equal success.

The present paper is devoted to a more detailed investigation of the reaction of aromatic aldehydes with ammonia and dialkyl hydrogen phosphites. It was first of all shown to what extent the reaction is a general one. We synthesized amino phosphonic acids from benzaldehyde, p-tolualdehyde, p-isopropylbenzaldehyde, p-anisaldehyde, piperonal, and vanillin. The reaction was carried out by heating equimolecular amounts of aldehyde and dialkyl hydrogen phosphite with a small excess of a 10% alcoholic solution of ammonia in sealed tubes in a water bath, and the corresponding esters of α-amino phosphonic acids were formed in accordance with the above equation. In order to isolate them from the reaction mixture, we converted these esters into well crystallizing salts—the hydrochloride or picrate. In Table 1 we give the salts of esters of α-amino phosphonic acids obtained in this way. From these salts of the esters the free acids were obtained by heating them with diluted (1 : 1) hydrochloric acid at 110-120° for several hours. The ester groups were then hydrolyzed, and when the solution was evaporated to dryness, the hydrochloride of the amino acid was converted into the internal salt with evolution of hydrogen chloride:

$$R \cdot CH \cdot PO(OR)_2 \xrightarrow[HCl]{H_2O} R \cdot CHPO(OH)_2 \longrightarrow R \cdot CH - PO(OH)O^- + HCl$$
$$|$$
$$NH_2 \cdot HCl \qquad\qquad NH_2 \cdot HCl \qquad\qquad N^+H_3$$
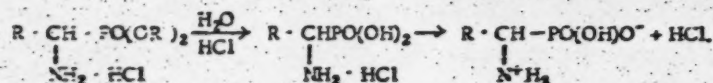
The free amino phosphonic acids obtained in this way are presented in Table 2. They are all high-melting crystalline solids, having powerful acid properties and titrating as monobasic acids.

With regard to the mechanism of the formation of amino phosphonic acids from aldehydes, dialkyl hydrogen phosphites, and ammonia, our first clue was provided by a study of the effect of the reaction temperature on the yield of amino phosphonic acid. When the reaction of aldehyde, dialkyl hydrogen phosphite, and ammonia is carried out not at 100°, but at a higher temperature, then in addition to the diester of the amino acid, some of the partially hydrolyzed product, the monoester, is formed. When, for example, piperonal was heated at 130-140° with alcoholic ammonia and diethyl hydrogen phosphite, not only the diethyl ester of the corresponding amino acid was formed, but also an acid ester of structure
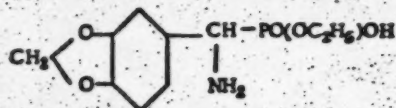

This substance was neutral and was converted into the free amino acid by hydrolysis. The formation of the monoester must undoubtedly be associated with the presence in the reaction mixture of water formed by reaction of ammonia with the aldehyde and the dialkyl hydrogen phosphite. When the reaction is carried out at room temperature, an insignificant amount of aminoalkylphosphonic ester is formed, the main product being a hydroxyalkylphosphonic ester (the case examined was benzaldehyde and diethyl hydrogen phosphite). Hence, in presence of
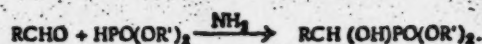
TABLE 1

Aldehyde	Dialkyl hydrogen phosphite	Salt isolated	M.p. (°C)	Yield %
C_6H_5CHO	$HPO(OC_2H_5)_2$	$C_6H_5CHPO(OC_2H_5)_2$ 　$\|$ 　$NH_2 \cdot HCl$	158-159	28
		$C_6H_5CHPO(OC_2H_5)_2$ 　$\|$ 　$NH_2HOC_6H_2(NO_2)_3$	174	—
	$HPO(OC_4H_9)_2$	$C_6H_5CHPO(OC_4H_9)_2$ 　$\|$ 　NH_2HCl	149	20
$CH_3C_6H_4CHO$-1,4	$HPO(OC_2H_5)$	$CH_3C_6H_4CHPO(OC_2H_5)_2$ 　$\|$ 　$NH_2 \cdot HCl$	149	8
		$CH_3C_6H_4CHPO(OC_2H_5)_2$ 　$\|$ 　$NH_2HOC_6H_2(NO_2)_3$	187	15
$(CH_3)_2CHC_6H_4CHO$-1,4	$HPO(OC_2H_5)_2$	$(CH_3)_2CHC_6H_4CHPO(OC_2H_5)_2$ 　$\|$ 　NH_2HCl	167	35
$CH_3OC_6H_4CHO$-1,4	$HPO(OC_2H_5)_2$	$CH_3OC_6H_4CHPO(OC_2H_5)_2$ 　$\|$ 　$NH_2 \cdot HCl$	160	32
$CH_2\genfrac{}{}{0pt}{}{O}{O}C_6H_2CHO$-1,3,4	$HPO(OC_2H_5)_2$	$CH_2\genfrac{}{}{0pt}{}{O}{O}C_6H_3CHPO(OC_2H_5)_2$ 　$\|$ 　$NH_2 \cdot HCl$	145	43
		$CH_2\genfrac{}{}{0pt}{}{O}{O}C_6H_3CH$ $PO(OC_2H_5)OH$ 　$\|$ 　NH_2	240	—
	$HPO(OC_4H_9)_2$	$CH_2\genfrac{}{}{0pt}{}{O}{O}C_6H_3CH$ $PO(OC_4H_9)_2$ 　$\|$ 　$NH_2 \cdot HCl$	160	14
$\genfrac{}{}{0pt}{}{CH_3O}{OH}C_6H_3CHO$-1,3,4	$HPO(OC_2H_5)_2$	$\genfrac{}{}{0pt}{}{CH_3O}{OH}C_6H_3CHPO(OC_2H_5)_2$ 　$\|$ 　$NH_2 \cdot HCl$	181	32

ammonia, dialkyl hydrogen phosphites react with aldehydes forming in the cold hydroxyalkylphosphonic ester, and at higher temperatures — aminoalkylphosphonic esters.

The formation of hydroxylakylphosphonic esters from dialkyl hydrogen phosphites and aldehydes under the catalytic action of sodium alkoxide has been studied by Abramov [10]. He showed that this reaction proceeds with evolution of heat in accordance with the equation

$$RCHO + HPO(OR')_2 \xrightarrow{R'ONa} R \cdot CH(OH) \cdot PO(OR')_2.$$
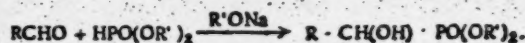
In our case ammonia evidently plays the part of basic catalyst:

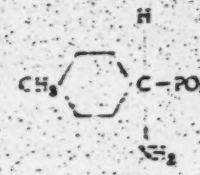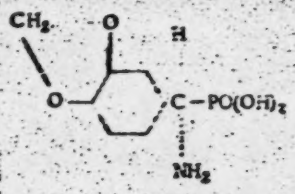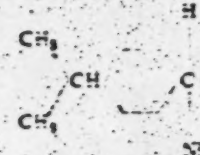$$RCHO + HPO(OR')_2 \xrightarrow{NH_3} RCH(OH)PO(OR')_2.$$
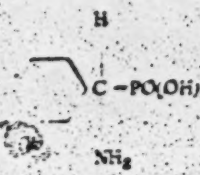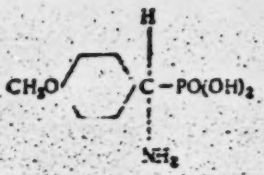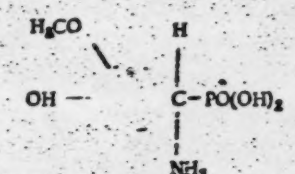
It was quite natural to suppose that hydroxyalkylphosphonic esters were formed as intermediate products in our synthesis of aminoalkylphosphonic esters, and that the second stage, which occurred when the mixture was heated, was the substitution reaction

$$RCH(OH)PO(OR')_2 + NH_3 \rightarrow RCH(NH_2)PO(OR')_2 + H_2O.$$
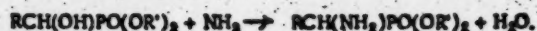
Such a supposition, however, is in conflict with the results of Fields [9], who in a discussion of the mechanism of the reaction of amines with aldehydes and dialkyl hydrogen phosphites states that hydroxyalkylphosphonic

TABLE 2

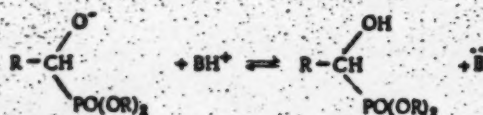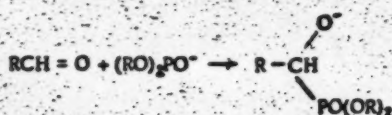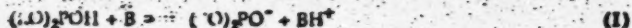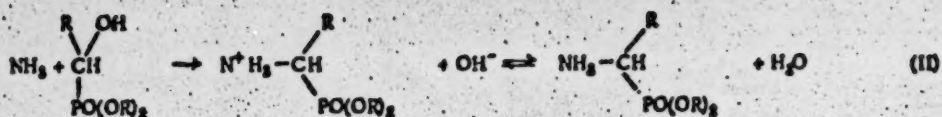| 1-Aminoalkylphosphonic acid	M p (°C)	Yield (%)	1-Aminoalkylphosphonic acid	M p (°C)	Yield (%)
(phenyl)C–PO(OH)$_2$, H, NH$_2$	273	72	CH$_3$O–(phenyl)C–PO(OH)$_2$, H, NH$_2$	268-269	85
CH$_3$–(phenyl)C–PO(OH)$_2$, H, NH$_2$	276	81	CH$_2$–O, O–(ring)C–PO(OH)$_2$, H, NH$_2$	255	35
CH$_3$–CH–C–PO(OH)$_2$, CH$_3$, H, NH$_2$	287	60	H$_3$CO, OH–(ring)C–PO(OH)$_2$, H, NH$_2$	215	81

acids do not react at all with amines at low temperatures (56.118°), whereas at high temperatures (175°) complete resinification of the reaction mixture occurs. For this reason we carried out our first experiments on the conversion of hydroxyalkylphosphonic acids into aminoalkylphosphonic acids in presence of sodium ethoxide as catalyst, and replacement of hydroxyl by amino was actually found to occur. It therefore appeared to be possible to synthesize the aminoalkylphosphonic acid as follows: first obtain dialkyl α-hydroxybenzylphosphonate from benzaldehyde and dialkyl hydrogen phosphite under Abramov's conditions, and then, without separating this from the reaction mixture, add an alcoholic solution of ammonia and heat in a sealed tube to convert the hydroxy ester into the amino ester. We did, in fact, carry out the synthesis of α-aminobenzylphosphonic acid by this method, but we later found that the use of a catalyst was unnecessary. As we have already mentioned, the formation of the ester of the hydroxy acid occurs readily in the cold in presence of ammonia. The second stage of the synthesis, replacement of hydroxyl by amino, occurs when the hydroxy ester is simply heated with alcoholic ammonia in a sealed tube to 100°.

These experiments reveal the mechanism of the formation of an aminoalkylphosphonic ester by the heating of benzaldehyde with a dialkyl hydrogen phosphite and alcoholic ammonia. It may be supposed that at first the most rapid reaction is the addition of the dialkyl hydrogen phosphite to the aldehyde under the catalytic action of ammonia, a hydroxybenzylphosphonic ester being formed. When this ester is heated with ammonia, hydroxyl is replaced by amino, and an aminobenzylphosphonic ester is formed. The whole process may be represented by the following equations (B = NH$_3$ or RO$^-$):

$$(RO)_2POH + B \rightleftharpoons (RO)_2PO^- + BH^+ \tag{1}$$

$$RCH = O + (RO)_2PO^- \rightarrow R-CH \begin{smallmatrix} O^- \\ PO(OR)_2 \end{smallmatrix}$$

$$R-CH \begin{smallmatrix} O^- \\ PO(OR)_2 \end{smallmatrix} + BH^+ \rightleftharpoons R-CH \begin{smallmatrix} OH \\ PO(OR)_2 \end{smallmatrix} + \ddot{B}$$

$$NH_3 + \underset{\underset{PO(OR)_2}{|}}{\overset{\overset{R \quad OH}{|\quad|}}{CH}} \longrightarrow N^+H_3 - \underset{\underset{PO(OR)_2}{|}}{\overset{\overset{R}{|}}{CH}} + OH^- \rightleftharpoons NH_2 - \underset{\underset{PO(OR)_2}{|}}{\overset{\overset{R}{|}}{CH}} + H_2O \qquad (II)$$
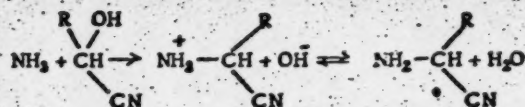
It is natural to compare the formation of aminoalkylphosphonic esters from aldehydes, ammonia, and dialkyl hydrogen phosphites with the well-known Zelinsky reaction, the formation of amino nitriles by the action of ammonium cyanide on aldehydes [11]. Here again we have a nucleophilic reagent, hydrocyanic acid, adding to a carbonyl group, and we have, in absence of ammonia:

$$RCH = O + \overline{C}N \longrightarrow R - \underset{\underset{CH}{|}}{\overset{\overset{O^-}{|}}{CH}} \longrightarrow RCH(OH)CN$$
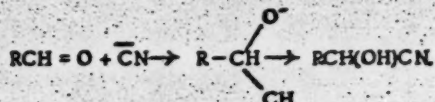
In presence of ammonia, however, not hydroxy nitriles, but amino nitriles are formed:

$$NH_3 + \underset{\underset{CN}{|}}{\overset{\overset{R \quad OH}{|\quad|}}{CH}} \longrightarrow \overset{+}{N}H_3 - \underset{\underset{CN}{|}}{\overset{\overset{R}{|}}{CH}} + OH^- \rightleftharpoons NH_2 - \underset{\underset{CN}{|}}{\overset{\overset{R}{|}}{CH}} + H_2O$$

It is known also that isolated hydroxy nitriles can be converted into amino nitriles by the action of alcoholic ammonia [12]:

$$RCH(OH)CN + NH_3 = RCH(NH_2)CN + H_2O$$
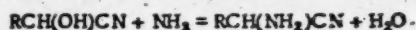
To the same type of reactions belongs, evidently, also Rodionov's reaction [13], in which the simultaneous action of ammonia and malonic acid on aldehydes leads to the formation of β-amino carboxylic acids:

$$NH_3 + RCHO + CH_2(COOH)_2 \longrightarrow \underset{\underset{NH_2}{|}}{RCH} - CH_2COOH + H_2O + CO_2.$$
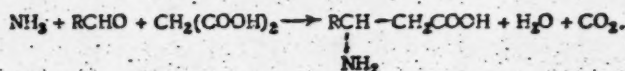
In a similar way, ammonium bisulfite adds to aldehydes with formation of α-amino sulfonic acids [14]:

$$NH_4HSO_2 + RCHO \longrightarrow R - \underset{\underset{SO_3H}{|}}{\overset{\overset{NH_2}{|}}{CH}}$$
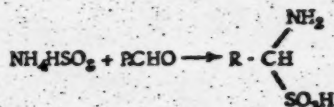
Dialkyl hydrogen phosphites in many of their reactions are reminiscent on the one hand of β-dicarbonyl compounds (malonic and acetoacetic esters) — an analogy which was examined systematically by Arbuzov [15] — and on the other hand of substances such as hydrocyanic and sulfurous acids, the diad tautomerism of which has been the subject of long discussions. In both cases, however, there is the possibility of obtaining two series of derivatives of the diad types. We may consider, on the basis of these comparisons, that the formation of α-amino-

substituted derivatives of the type $R - \underset{\underset{X}{|}}{\overset{\overset{NH_2}{|}}{CH}}$ by the action of aldehydes and ammonia is a general reaction for

all substances HX that are weak acids and are able to show dual reactivity of the diad or triad type.

EXPERIMENTAL

Hydrochloride of Diethyl α-Aminobenzylphosphonate. A mixture of 6 g of benzaldehyde, 8 g of diethyl hydrogen phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a

boiling water bath for seven hours. The reaction mixture was then evaporated down on a boiling water bath until a constant residue was obtained. The residue, a yellowish sirup, was dissolved in a small amount of absolute ethanol, and dry ether was added until a turbidity appeared. The solution was cooled with ice water, and dry hydrogen chloride was passed. The precipitate that formed was filtered off and washed with dry ether. The colorless crystals obtained were readily soluble in water, methanol, and ethanol, and insoluble in benzene, acetone, and ether. The substance was crystallized from dioxane in the form of fine colorless needles, and these melted with decomposition at 155-159°. The yield was 6 g (38%).

Found %: N 5.0; 4.9; P 11.0, 11.1; Cl 12.3; 12.4

$C_{11}H_{19}NPO_3Cl$. Calculated %: N 5.0; P 11.1; Cl 12.7

Hydrochloride of Dibutyl a-Aminobenzylphosphonate. This was prepared similarly to the preceding substance from 10 6 g of benzaldehyde, 19.4 g of dibutyl hydrogen phosphite, and 40 ml of a 7% solution of ammonia in absolute butyl alcohol. The substance was readily soluble in water and methanol, and could be crystallized from ethanol or dioxane: m.p. 149°: yield 6.7 g (20%).

Found %: C 53.2; 53.2; H 7.8; 8.1; N 4.4; 4.1; P 9.1; 9.0

$C_{15}H_{25}NPO_3Cl$. Calculated %: C 53.7; H 8.1; N 4.2; P 9.3

Picrate of Diethyl a-Aminobenzylphosphonate. The hydrochloride of diethyl a-aminobenzylphosphonate (3 5 g. m.p. 155°) was treated with a 3% aqueous solution of NaHCO$_3$, and the solution obtained was extracted with ether. The ether solution was dried over sodium sulfate, and the ether was driven off. The residue was a yellowish oily liquid (diethyl a-aminobenzylphosphonate), which it was not found possible to purify. It was dissolved in dry ether, and an ethereal solution of picric acid was added. A yellow crystalline precipitate, m.p. 174°, was obtained.

Found %: N (in NH$_2$) 2.7; 2.6; P 6.9; 6.6

$C_{17}H_{21}N_4PO_{10}$. Calculated %: N 3.0; P 6.6

a-Aminobenzylphosphonic Acid. A mixture of 2 g of the hydrochloride of diethyl a-aminobenzylphosphonate and 50 ml of hydrochloric acid (1 : 1) was heated in a sealed tube at 120-140° for three hours. The reaction mixture was evaporated down on a boiling water bath until the odor of hydrochloric acid disappeared. The dry residue was recrystallized from a mixture of water and alcohol, and yielded 0.9 g (72%) of a colorless crystalline substance. m.p. 272-273°.

Found %: C 45.4; 45.5; H 5.3; 5.4; N 7.9; 7.7; P 16.6; 16.7

$C_7H_{10}PNO_3$. Calculated %: C 44.9; H 5.4; N 7.5; P 16.6

Hydrochloride of Diethyl a-Amino-p-methylbenzylphosphonate. This was prepared from 5.5 g of p-tolualdehyde, 5 5 g of diethyl hydrogen phosphite, and 13.5 ml of a 10% solution of ammonia in absolute ethanol, the procedure being as in the experiment with benzaldehyde The hydrochloride, which was precipitated with ether, was recrystallized after five days from a mixture of alcohol and ether, and yielded 1.1 g (8%) of product, which melted with decomposition at 148°.

Found %: C 49.4; 49.1; H 7.4; 7.3; N 4.9; 4.8; P 10.7; 10.8

$C_{12}H_{21}NPClO_3$. Calculated %: C 49.1; H 7.2; N 4.8; P 10.6

Picrate of Diethyl a-Amino-p-methylbenzylphosphonate. A mixture of 6 g of p-tolualdehyde, 7 g of diethyl hydrogen phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water-bath for seven hours. The reaction mixture was evaporated down on a boiling water bath, and the residue was extracted with ether. To the solution obtained an ethereal solution of picric acid was added, and the crystals that were precipitated were filtered off (3.95 g, i.e., 16%). The substance, after recrystallization from ethanol, melted with decomposition at 187°.

Found %: C 44.1; 44.3; H 5.2; 5.0; N (in NH$_2$) 2.8; 2.7; P 6.6; 6.5

$C_{18}H_{23}N_4PO_{10}$. Calculated %: C 44.4; H 4.8; N 2.9; P 6.4

a-Amino-p-methylbenzylphosphonic Acid. A. A mixture of 3.2 g of the picrate of diethyl a-amino-p-methylbenzylphosphonate and hydrochloric acid (1 1; 60 ml) was heated in sealed tubes at 110-120° for three hours The reaction mixture was extracted with ether, and the aqueous solution was evaporated down. The residue was recrystallized from water, and yielded 0.5 g of product, m.p. 276°.

Found %: C 48.2; 48.3; H 5.8; 6.0; N 6.8; 6.7; P 15.5; 15.5

$C_8H_{12}NPO_3$. Calculated %: C 47.8; H 6.0; N 7.0; P 15.4

B. A mixture of 0.9 g of the hydrochloride of diethyl α-amino-p-methylbenzylphosphonate and 25 ml of hydrochloric acid (1 : 1) was heated in a sealed tube at 110° for three hours. The contents of the tube were evaporated down, and the residue was recrystallized from water, yielding 0.5 g (81%) of product, m.p. 276°.

Hydrochloride of Diethyl α-Amino-p-isopropylbenzylphosphonate. This was prepared from 7.4 g of p-isopropylbenzaldehyde, 8.3 g of diethyl hydrogen phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol, the procedure being as in the experiment with benzaldehyde. The product was recrystallized from absolute ethanol, and yielded 5.6 g (35%) of colorless crystals, melting with decomposition at 167°.

<div align="center">

Found %: N 4.4; 4.5; P 9.4; 9.5

$C_{14}H_{25}NPClO_3$ Calculated %: N 4.4;   P 9.6;

</div>

α-Amino-p-isopropylbenzylphosphonic Acid. This was prepared from 4.5 g of the hydrochloride of diethyl α-amino-p-isopropylbenzylphosphonate and 50 ml of hydrochloric acid (1 : 1) by heating them together in sealed tubes at 110-120° for three hours. After the evaporation, the residue was recrystallized from water, yielding 1.9 g (60%) of a colorless crystalline substance, which melted with decomposition at 267°.

<div align="center">

Found %: C 52.5; 52.3; H 7.1; 6.9; N 6.1; 6.2; P 13.9; 13.8

$C_{10}H_{16}NPO_3$ Calculated %: C 52.4;   H 7.0;   N 6.1;   P 13.5

</div>

Hydrochloride of Diethyl α-Amino-p-methoxybenzylphosphonate. This was prepared from 4.1 g of p-anisaldehyde, 4.15 g of diethyl hydrogen phosphite, and 7.5 ml of a 10% solution of ammonia in absolute ethanol. The substance was reprecipitated from a mixture of ether and alcohol, and 3 g (32%) of white crystals, m.p. 160°, was obtained.

<div align="center">

Found %: C 46.9; 46.5; H 6.9; 6.9; Cl 11.6; 11.6; P 10.2; 10.3; N 4.2; 4.4

$C_{12}H_{21}NPO_4Cl.$ Calculated %: C 46.7;   H 6.8;   Cl 11.5;   P 10.2;   N 4.5

</div>

α-Amino-p-methoxybenzylphosphonic Acid. A mixture of 1 g of the hydrochloride of diethyl α-amino-p-methoxybenzylphosphonate and 20 ml of hydrochloric acid (1 : 1) was heated in a sealed tube in a boiling water bath for six hours. Recrystallization from water yielded 0.55 g (85%) of a colorless crystalline substance, m.p. 278-279°.

<div align="center">

Found %: N 6.2; 6.2; P 14.2; 14.5

$C_8H_{12}NPO_4$ Calculated %: N 6.4;   P 14.3

</div>

Hydrochloride of Diethyl α-Amino-3,4-methylenedioxybenzylphosphonate. This was prepared from 4.5 g of piperonal, 4.2 g of diethyl hydrogen phosphite, and 20 ml of an ethanolic solution of ammonia. The product could be recrystallized from dioxane and reprecipitated from a mixture of alcohol and ether; it melted with decomposition at 145°. The yield was 4.2 g (43%).

<div align="center">

Found %: C 44.3; 44.2; H 6.1; 6.2; N 4.4; 4.3; P 9.2; 9.4; Cl 10.3; 10.6

$C_{12}H_{19}NPO_5Cl.$ Calculated %: C 44.5;   H 5.9;   N 4.3;   P 9.6;   Cl 10.9

</div>

Ethyl Hydrogen α-Amino-3,4-methylenedioxybenzylphosphonate. A mixture of 4.5 g of piperonal, 4.2 g of diethyl hydrogen phosphite, and 20 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes at 130-140° for five hours. The reaction mixture was evaporated down on a boiling water bath until a constant residue was obtained. The residue was transferred to some absolute ethanol, and the crystals remaining undissolved were filtered off and recrystallized from a mixture of water and alcohol. The product was 0.4 g (5%) of a water-soluble substance, m.p. 240°.

<div align="center">

Found %: C 46.2; 46.3; H 5.9; 5.9; N 5.5; 5.4; P 11.9; 11.7

$C_{10}H_{14}NPO_5$ Calculated %: C 46.3;   H 5.4;   N 5.4;   P 11.9

</div>

The alcoholic filtrate was saturated with dry hydrogen chloride and then treated exactly as in the preceding experiment. From the filtrate 0.3 g of ammonium chloride and 2.0 g (21%) of the hydrochloride of diethyl α-amino-3,4-methylenedioxybenzylphosphonate were isolated.

Hydrochloride of Dibutyl α-Amino-3,4-methylenedioxybenzylphosphonate. Prepared from 4.5 g piperonal, 5.8 g dibutyl hydrogen phosphite, and 10 ml of a 7% solution of ammonia in absolute butyl alcohol, the mixture being heated in sealed tubes in a boiling water bath for ten hours. The product was recrystallized from butyl alcohol, and 1.0 g (14%) was obtained of a substance that exhibited two melting points, 160° and 214°.

<div align="center">

Found %: C 49.8; 50.7; H 7.4; 7.4; Cl 9.8; 9.6; P 8.4; 8.0; N 3.6; 3.6

$C_{16}H_{27}O_5PNCl.$ Calculated %: C 50.6;   H 7.1;   Cl 9.4;   P 8.2;   N 3.7

</div>

a-Amino-3,4-methylenedioxybenzylphosphonic Acid. A mixture of 2 g of the hydrochloride of diethyl a-amino-3,4-methylenedioxybenzylphosphonate, m.p. 145°, and 40 ml of hydrochloric acid (1 : 1) was heated in a sealed tube in a boiling water bath for seven hours. The reaction mixture was evaporated down, and the residue was crystallized from water, yielding 0.5 g (35%) of a substance of m.p. 255°.

Found %: C 41.3; 41.3; H 4.5; 4.4; N 6.5; P 13.4; 13.5
$C_8H_{10}NPO_5$ Calculated %: C 41.5;   H 4.3;   N 6.1, P 13.4

Hydrochloride of Diethyl a-Amino-4-hydroxy-3-methoxybenzylphosphonate. This was prepared from 7.2 g of vanillin, 8.3 g of diethyl hydrogen phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol. Recrystallization of the product from absolute ethanol yielded 5 g (32%) of a substance that melted with decomposition at 181°.

Found %: C 44.4; 44.2; H 6.6; 6.8; P 9.8; 9.7; N 4.1; 4.2 Cl 10.8; 11.3
$C_{12}H_{21}NPClO_5$ Calculated %: C 44.2;   H 6.5;   P 9.5;   N 4.3   Cl 10.9

a-Amino-4-hydroxy-3-methoxybenzylphosphonic Acid. This was prepared from 5 g of the hydrochloride of diethyl a-amino-4-hydroxy-3-methoxybenzylphosphonate and 120 ml of hydrochloric acid (1 : 1), the mixture being heated in sealed tubes in a boiling water bath for three hours. Recrystallization of the product from water yielded 3.5 g (81%) of substance of m.p. 215°.

Found %: N 6.0; 6.1; P 13.2, 13.1
$C_8H_{12}NPO_5$ Calculated %: N 6.0;   P 13.3

Diethyl a-Hydroxybenzylphosphonate. A mixture of 6 g benzaldehyde, 8 g diethyl hydrogen phosphite, and 25 ml of a 10% solution of ammonia in absolute ethanol was sealed in tubes and set aside at room temperature for twelve days. The contents of the tubes were then evaporated down in a dish on a boiling water bath until a constant residue was obtained. On being cooled, the residue in the dish crystallized out, and the crystals obtained were washed with dry ether. The product was 5.9 g (43%) of a white crystalline substance, which melted, after recrystallization from petroleum ether, at 83-84°. In admixture with the diethyl a-hydroxybenzylphosphonate obtained by Kabachnik and Rossyskaya [6] it showed no depression of melting point.

Found %: C 54.5; 54.3; H 7.1; 7.2; P 12.9; 13.0
$C_{11}H_{17}PO_4$ Calculated %: C 54.1;   H 7.0;   P 12.7

The ether filtrate was saturated with dry hydrogen chloride, and the precipitated substance was filtered off, yielding 2.0 g (12%) of the hydrochloride of diethyl a-aminobenzylphosphonate.

Reaction of Diethyl a-Hydroxybenzylphosphonate with Ammonia (in Presence of Sodium Ethoxide). A mixture of 2.44 g of diethyl a-hydroxybenzylphosphonate (m.p. 82-83°), 3 ml of a 10% solution of ammonia in absolute ethanol, and a solution of 0.023 g of sodium in 2 ml of ethanol was heated in a sealed tube in a boiling water bath for seven hours. The substance obtained was reprecipitated from a mixture of alcohol and ether. The product (0.7 g, i.e., 25%) melted at 159°.

Found %: N 4.9; P 10.8; 10.6
$C_{11}H_{19}NPO_3Cl$ Calculated %: N 5.0; P 11.1

Reaction of Diethyl a-Hydroxybenzylphosphonate with Ammonia (in Absence of Catalyst). A mixture of 2.35 g of diethyl a-hydroxybenzylphosphonate and 6 ml of a 10% solution of ammonia in absolute ethanol was heated in a sealed tube in a boiling water bath for seven hours. Recrystallization of the product from dioxane, yielded 1.6 g (27%) of a substance of m.p. 158°.

Found %: N 4.8; 5.0
$C_{11}H_{19}NPO_3Cl$ Calculated %: N 5.0

Preparation of the Hydrochloride of Diethyl a-Aminobenzylphosphonate via Diethyl a-Hydroxybenzylphosphonate. Sodium methoxide (20 drops) was added to a mixture of 5 g of benzaldehyde and 6.9 g of diethyl hydrogen phosphite, and the temperature of the mixture rose to 50°. The mixture was then heated in a boiling water bath for 30 minutes, and cooled. An addition was made of 15 ml of a 10% solution of ammonia in absolute ethanol, and the mixture was heated in sealed tubes in a boiling water bath for seven hours. The further treatment of the reaction mixture was carried out in the manner described for the experiment on the reaction of diethyl a-hydroxyphosphonate with ammonia. The product was 4 g (30%) of the hydrochloride of diethyl a-aminobenzylphosphonate, m.p. 155°.

SUMMARY

1. The reaction of aldehydes with dialkyl hydrogen phosphites and ammonia has been investigated, and it has been established that when heat is applied a-aminoalkylphosphonic esters are formed; on hydrolysis these yield the free acids.

2. By this method a-amino phosphonic acids have been synthesized from benzaldehyde, p-tolualdehyde, p-isopropylbenzaldehyde, p-anisaldehyde, piperonal, and vanillin.

3. It has been shown that benzaldehyde reacts with dialkyl hydrogen phosphites and ammonia in the cold with formation of a-hydroxybenzylphosphonic esters, which, on being heated with ammonia, are converted into a-aminobenzylphosphonic esters.

4. A mechanism has been proposed for the reaction, in which a-hydroxyalkylphosphonic esters play the part of intermediate products. A parallel has been drawn between the reaction observed and other reactions: Zelinsky's reaction, Rodionov's reaction, and the formation of a-amino sulfonic acids from aldehydes and ammonium bisulfite.

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HIGH-TEMPERATURE CONTACT-CATALYSIS REACTIONS OF NORMAL ALKANES

IN PRESENCE OF HYDROGEN AT HIGH PRESSURE

N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov

We have previously studied contact-catalysis reactions of cyclopentanes and cycloalkanes under conditions of high temperature and pressure [1]. It was then shown that at 460° under a hydrogen pressure of 15-20 atm, cyclopentane, methycyclopentane, and cyclohexane underwent a number of far-reaching changes in presence of a platinized alumina catalyst, the products being aromatic hydrocarbons, alkylation and isomerization products, and a considerable amount of paraffins of normal and branched structures.

It was considered to be of interest to examine the transformations, under the same conditions, of normal alkanes (hexane, heptane, and octane). In these experiments it was proposed to obtain data that would permit a comparative examination of the behavior of these normal alkanes in its relation to their molecular weights, and would enable the mechanism of the formation of branched paraffins and aromatic hydrocarbons under the given conditions to be elucidated.

EXPERIMENTAL

The hexane, heptane, and octane taken for the investigation were obtained by dehydration of the corresponding primary alcohols at 360° in presence of alumina, followed by hydrogenation of the alkenes obtained in presence of a nickel catalyst. The hydrocarbons were purified by careful distillation through a 35-plate column.

Catalytic Treatment of Hexane

The hexane used had the following properties: b.p. 68.8° (750 mm); n_D^{25} 1.3765; d_4^{29} 0.6697; Found MR_D 29.97; Calculated MR_D for C_6H_{14} 30.21.

This hydrocarbon (780 ml, i.e., 514.6 g) was passed at 460° over a platinized alumina catalyst at a space velocity of 0.43 under a pressure of 20 atm of hydrogen. As a result 355.3 g (528.6 ml) of catalyzate was obtained; it boiled over the range 27.5-87, had n_D^{25} 1.3840; d_4^{29} 0.6721, and contained 7% of aromatic hydrocarbons. The yield was 69% on the amount of hexane taken.

Distillation of 35.6 g of the catalyzate over sodium through a column yielded a residue of 0.65 g, which boiled over the range 87-153° at 749 mm. This residue was subjected to Ullmann permanganate oxidation, and from the resulting mixture [2] 0.0097 g of pure benzoic acid, m.p. 121.6° and 0.1505 g of a mixture of benzene-dicarboxylic acids, m.p. 290-292°, were isolated. In order to avoid loss of the highly volatile components of the catalyzate, the remaining bulk of it was fractionated through a 70-plate column in order to obtain the hydrocarbons boiling up to 38° at 752 mm, and the following fractions were obtained:

Fraction I, b.p. 27-28.0°; 10.5 ml (6.5 g); n_D^{20} 1.3545; d_4^{20} 0.6203
Fraction II, b.p. 35-35.6°; 12 ml (7.5 g); n_D^{20} 1.3570; d_4^{20} 0.6278

Comparison of the properties of these fractions with data in the literature for 2-methylbutane and pentane showed that they consisted, respectively, of these hydrocarbons.

After the isopentane and pentane had been removed from the catalyzate, aromatic hydrocarbons were removed by treatment with 3% oleum; the catalyzate residue then had n_D^{20} 1.3760; and d_4^{20} 0.6586. For fractionation through the 70-plate column, 125.6 g (190.6 ml) of the catalyzate was taken, and the results of the fractionation are presented in Table 1 and Fig. 1. The gas that was isolated in the various trials contained from 78 to 88% of hydrogen, the remainder being saturated hydrocarbons; for example, the analysis of the gas from Trial No. 7 was: 79.2% of hydrogen, 20.8% of saturated hydrocarbons.

TABLE 1

Fractional Composition of the Paraffin Part of the Hexane Catalyzate

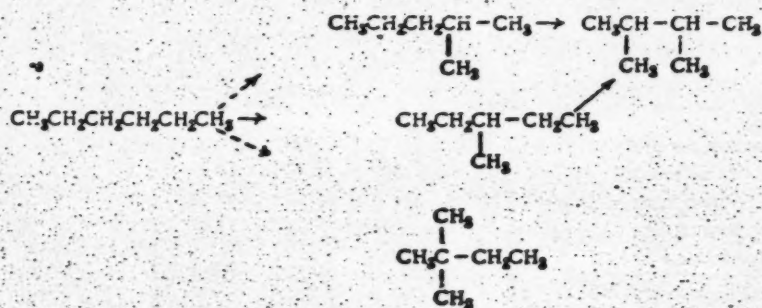| Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%)		
					on catalyzate	on hexane taken	on mixture of alkanes taken for fractionation
I	48.5-50.5	3.6	1.3670	0.6478	1.5	1.0	2.8
II	50.5-59.5	21.8	1.3715	0.6526	15.8	10.7	17.3
III	59.5-61.5	16.0	1.3710	0.6532	11.5	7.9	12.7
IV	61.5-63.0	1.4	1.3760	–	0.7	0.5	1.1
V	63.0-64.0	19.9	1.3760	0.6641	14.0	9.7	15.8
VI	64.0-68.5	2.0	1.3760	–	0.8	0.5	1.6
VII	68.5	53.4	1.3765	0.6590	38.7	26.7	42.5
	Residue	6.6	1.3765	0.6597	5.1	3.5	5.3
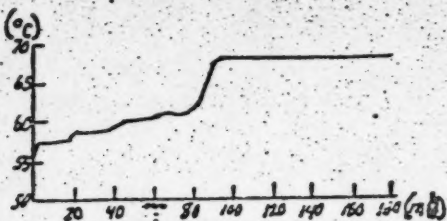
Fig. 1. Fractionation curve for the paraffin part of the hexane catalyzate.

Comparison of the properties of Fraction I of the paraffin part of the catalyzate with data in the literature for 2,2-dimethylbutane showed that it consisted mainly of this hydrocarbon. It was evident from an examination of the properties of Fraction II that it consisted mainly of 2,3-dimethylbutane, and optical analysis of it showed * that it contained 95% of 2,3-dimethylbutane and about 5% of 2,2-dimethylbutane. Fractions III, IV, and V consisted of mixtures of 2- and 3-methylpentane. Fraction VII was unchanged hexane.
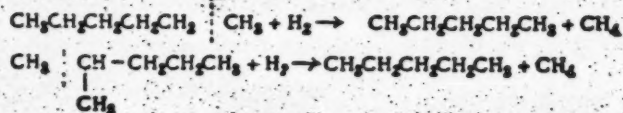
Under these conditions, therefore, hexane undergoes the following transformations: part of it (about 10%) is converted as a result of dehydrocyclization into benzene:

$$CH_2CH_2CH_2CH_2CH_2CH_2 \longrightarrow \text{[benzene]} + 4H_2$$
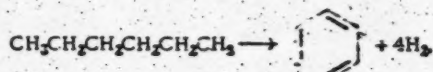
and the main bulk of it isomerizes into branched hexane isomers (2- and 3-methylpentanes, 2,3- and 2,2-dimethylbutanes):

$$CH_3CH_2CH_2CH-CH_3 \rightarrow CH_3CH-CH-CH_3$$
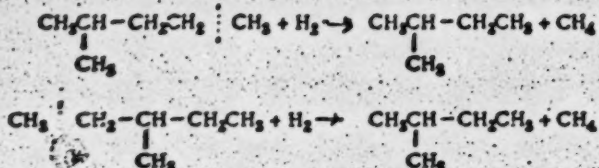$$\quad\quad\quad | \quad\quad\quad\quad | \quad |$$
$$\quad\quad\quad CH_3 \quad\quad\quad CH_3 \ CH_3$$

$$CH_3CH_2CH_2CH_2CH_2CH_3 \rightarrow$$

$$CH_3CH_2CH-CH_2CH_3$$
$$\quad\quad\quad |$$
$$\quad\quad\quad CH_3$$

$$\quad\quad CH_3$$
$$\quad\quad |$$
$$CH_3C-CH_2CH_3$$
$$\quad\quad |$$
$$\quad\quad CH_3$$

At the same time hydrogenolysis reactions occur with formation of pentane:

$$CH_3CH_2CH_2CH_2CH_2 \,\vdots\, CH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3 + CH_4$$

$$CH_3 \,\vdots\, CH-CH_2CH_2CH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3 + CH_4$$
$$\quad\quad |$$
$$\quad\quad CH_3$$

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* Optical analyses were carried out on 12 fractions of the catalyzates from the three investigated alkanes by M. I. Batuev, to whom we express our thanks.

and 2-methylbutane:

$$CH_3CH-CH_2CH_2 \vdots CH_3 + H_2 \rightarrow CH_3CH-CH_2CH_3 + CH_4$$
$$\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\quad CH_3 \qquad\qquad\qquad\qquad\qquad\quad CH_3$$

$$CH_3 \vdots CH_2-CH-CH_2CH_3 + H_2 \rightarrow CH_3CH-CH_2CH_3 + CH_4$$
$$\qquad\qquad\qquad | \qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad CH_3 \qquad\qquad\qquad\qquad\qquad CH_3$$

A considerable amount (about 30%) of the substance (the original hexane and its transformation products) undergoes cracking with formation of gaseous alkanes. The formation of small amounts of toluene and xylenes shows that, in this case also, the breakdown of hydrocarbons (hexane, the products of its isomerization and hydrogenolysis, and cyclohexane formed intermediately by the dehydrocyclization of hexane) is accompanied by the formation of methylene radicals, most of which are hydrogenated to methane $CH^{\cdot}_2 + H_2 \rightarrow CH_4$, while the remainder methylate benzene:

$$+ CH^{\cdot}_2 \rightarrow \qquad -CH_3$$

$$-CH_3 + CH^{\cdot}_2 \rightarrow C_6H_4(CH_3)_2$$
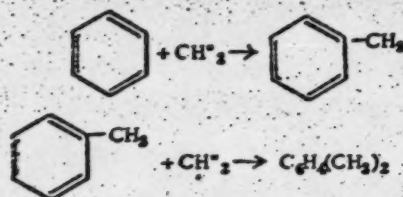
The results obtained show that the main direction in the contact-catalysis reactions of hexane under the conditions investigated is its isomerization into the corresponding branched paraffins having one or two tertiary carbon atoms. 2,2-Dimethylbutane is formed only to a slight extent. Also, dehydrocyclization occurs to an appreciable extent.

Catalytic Treatment of Heptane

The transformation of heptane b.p. 98.3° (751 mm); n_D^{20} 1.3876; d_4^{20} 0.6829; were studied in presence of the same catalyst at 469° under an excess pressure of hydrogen of 15 atm. For the catalytic reaction, 800 ml (545.3 g) of heptane was taken, and it was passed through the catalysis tube at a space velocity of 0.43. The catalyzate (501.7 ml, i.e., 345.9 g) had n_D^{20} 1.4035; d_4^{20} 0.6895, and contained 18% by volume of aromatic hydrocarbons. The yield was 63.3%. As in the case of hexane, before separation of aromatic hydrocarbons, 2-methylbutane and pentane were removed from the catalyzate through a 70-plate column. These hydrocarbons had the following properties: 2-methylbutane, b.p. 27.6-28° (742 mm), n_D^{20} 1.3536; d_4^{20} 0.6201; pentane, b.p. 35-35.6° (742 mm), n_D^{20} 1.3575; d_4^{20} 0.6280.

The aromatic hydrocarbons were separated from the catalyzate by the chromatographic method. For the adsorption, 285 ml (196.5 g) of catalyzate freed from 2-methylbutane and pentane was taken, and the aromatic hydrocarbons separated (56.0 ml, i.e., 48.4 g) had n_D^{20} 1.4980 and d_4^{20} 0.8654. They were fractionated through a 35-plate column, with the results shown in Table 2.

Ullmann oxidation of the toluene-xylene fraction (V, 110.5-138°) yielded 2.4 g of a mixture of carboxylic acids, from which, apart from a trace of benzoic acid, the following acids were isolated: 0.6071 g of phthalic acid (converted into phthalic anhydride; m.p. 130.8°), 1.2740 g of isophthalic acid (converted into the dimethyl ester, m.p. 66.8°), and 0.3085 g of terephthalic acid (identified via the dimethyl ester, m.p. 140°). The residue (6.4 g) (n_D^{20} 1.5480) was distilled from a flask having a Vigreux column; at 752 mm it distilled over a wide range of temperature (150-243°).

It follows from the results given in Table 2 that the aromatic part of the heptane catalyzate contained, in addition to toluene (69.8%), appreciable amounts of benzene, xylenes, and also, in the residue, evidently polymethylbenzenes. It is possible that the presence of xylene and polymethylbenzenes resulted from the methylation of benzene by methylene radicals formed under our experimental conditions.

The paraffin part of the catalyzate (228.5 ml, i.e., 155.1 g; n_D^{20} 1.3895 and d_4^{20} 0.6787) was subjected to precise fractionation through a 70-plate column. The results of the fractionation and the properties of the fractions collected are shown in Table 3 and Fig. 2.

TABLE 2

General Composition of Aromatic Hydrocarbons in the Hexane Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{23}	d_4^{20}	Yield (%)	
					on catalyzate	on mixture of aromatic hydrocarbons taken
I	to 80.0	1.3	1.4920	–	0.7	2.3
II	80.0-80.5	2.0	1.4995	0.8782	1.0	4.0
III	80.5-109.8	1.4	1.4970	–	0.7	2.8
IV	109.8-110.5	33.8	1.4965	0.8070	17.2	69.8
V	110.5-138	3.0	1.4970	0.8750	1.5	6.2
	Residue	6.4	1.5489	–	3.3	13.1

TABLE 3

Fractional Composition of the Paraffin Part of the Hexane Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%)		
					on catalyzate	on heptane taken	on mixtures of alkanes taken for fractionation
I	46.5-59.5	7.9	1.3721	0.6580	4.3	2.9	5.1
II	59.5-76.0	6.7	1.3765	0.6615	4.2	2.8	4.3
III	76.0-87.0	8.6	1.3860	0.6617	4.6	3.1	5.4
IV	87.0-89.5	16.6	1.3830	0.6795	8.7	5.9	10.7
V	89.5-91.5	24.5	1.3890	0.6929	12.9	8.8	15.5
VI	91.5-92.0	17.7	1.3855	0.6875	9.2	6.3	11.4
VII	92.0-97.5	22.4	1.3880	0.6881	11.9	6.9	14.4
VIII	97.5-98.8	34.5	1.3876	0.6841	17.9	12.2	21.2
	Residue	9.6	1.3890	0.6843	4.9	3.4	6.2

Fig. 2 Fractionation curve for the paraffin part of the hexane catalyzate.

The results of the fractionation of the paraffin part of the heptane catalyzate and comparisons of the properties of the fractions with those of individual hydrocarbons show that the transformations of heptane are similar to those of hexane: in this case the main reactions are isomerization to 2- and 3-methylhexanes, fission reactions, and aromatization. Comparison of the properties of Fraction I with the data in the literature for 2,2-dimethylbutane indicates that this hydrocarbon forms the bulk of the fraction.

Fraction II and united Fractions III and IV were investigated by the Raman spectrum method, and this indicated that Fraction II contained 55% of 2-methylpentane and 45% of 2,2-dimethylpentane, and that united Fractions III and IV contained 48% of 2,2-dimethylpentane and 52% of 2,4-dimethylpentane. The properties of Fraction V indicated it was a mixture of 3,3- and 2,3-dimethylpentanes; Fractions VI and VII consisted mainly of 2- and 3-dimethylhexanes; and Fraction VIII contained unchanged heptane.

Analysis of the gas evolved showed that it contained a rather higher amount of saturated hydrocarbons than the gas obtained from hexane. Thus, in various trials the saturated-hydrocarbon content varied from 22 to 25%.

The investigation of the heptane catalyzate showed that, in presence of a platinized alumina catalyst at 460° under 15 atm of hydrogen, part of the original hydrocarbon underwent dehydrocyclization with formation of toluene:

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_3 \longrightarrow \text{(toluene)} + 4H_2$$

The observed formation of xylenes and more complex benzene homologs is evidently to be explained in this case also by the methylation of toluene by methylene radicals that are formed under our experimental conditions.

Many of these radicals are converted into methane: $CH_2^* + H_2 \rightarrow CH_4$, and the remainder react with toluene with formation of xylenes and more complex methylation products:

$$C_6H_5-CH_3 + CH_2^* \rightarrow C_6H_4(CH_3)_2;$$
$$C_6H_4(CH_3)_2 + nCH_2^* \rightarrow C_6H_{4-n}(CH_3)_{n+2}.$$
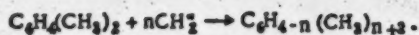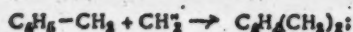
The results of the contact-catalysis transformations of hexane and heptane show that methylene radicals arise not only as a result of the fission of cycloalkanes (which are formed, in this case, only intermediately), but also in the methane breakdown of alkanes. The greater part of the heptane undergoes isomerization with formation of 2- and 3-methylhexanes and 2,3-, 2,4-, 2,2-, and 3,3-dimethylpentanes:
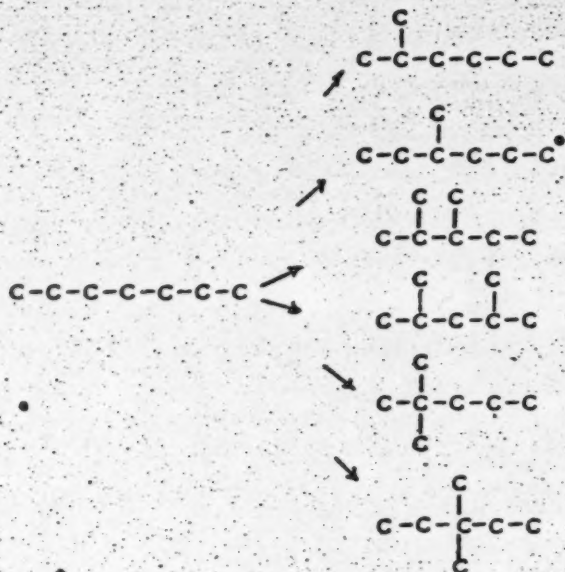
In addition to dehydrocyclization, methylation, and isomerization, hydrogenolysis occurs also, both of the paraffins and of the benzene homologs:
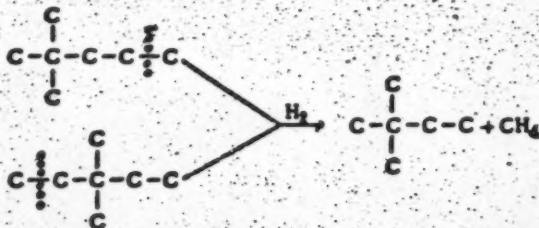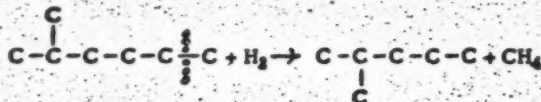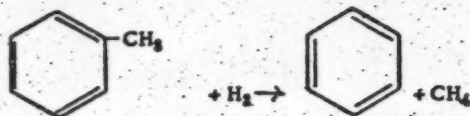
The experiments were carried out with 850 ml (597.8 g) of octane having the following constants: n_D^{20} 1.3980; d_4^{20} 0.7033, b.p. 125-126° (753 mm); Found MR_D 39.30, Calculated C_8H_{18} for MR_D 39.14. The catalytic treatment was carried out under the same conditions as those of the heptane experiments, and 492.3 ml (381.5 g, i.e., 63.9%) of catalyzate was obtained; it had the boiling range 27-159°, had n_D^{20} 1.4260; d_4^{20} 0.7748, and contained 30% of aromatic hydrocarbons. In the same way as in the previous experiments, fractions boiling up to 37° at 758 mm were distilled off:

Fraction I, b.p. 27.5-28°; 14.5 ml (9.1 g); n_D^{20} 1.3545, d_4^{20} 0.6201 (yield on octane taken 1.5%)
Fraction II, b.p. 28-35.5°, 0.1 ml
Fraction III, b.p. 35.5-37°, 16 ml (10.0 g); n_D^{20} 1.3576; d_4^{20} 0.273; yield 1.7.

By adsorption of silica gel 86.1 ml (73.8 g) of aromatic hydrocarbons of n_D^{20} 1.4975 and d_4^{20} 0.8673 was isolated from 290 ml (229.1 g) of catalyzate freed from highly volatile components. It was fractionated through a 70-plate column (73.6 ml, i.e., 63.0 g of the aromatic hydrocarbons was taken for the fractionation). The results of the fractionation are shown in Table 4 and Fig. 3.

TABLE 4

Fractional Composition of Aromatic Hydrocarbons Isolated from the Octane Catalyzate.

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield (%)	
					on catalyzate	on mixture taken for fractionation
I	to 79.5	1.7	1.4860	—	0.9	2.7
II	79.5-80.3	1.2	1.4980	0.8780	0.6	1.2
III	80.3-109.8	0.5	1.4970	—	0.2	0.9
IV	109.8-110.5	5.6	1.4960	0.8672	2.6	8.8
V	110.5-137.6	0.7	1.4965	—	0.3	1.1
VI	137.6-138.6	27.8	1.4970	0.8625	14.2	44.1
VII	138.6-144.2	17.9	1.4997	0.8709	8.9	28.1
	Residue	7.1	1.5690	0.8892	3.4	11.3

The paraffin part of the octane catalyzate was fractionated through the same column; the results are presented in Table 5 and Fig. 4.
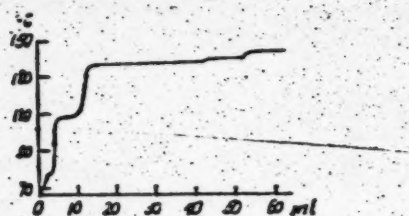

Fig. 3. Fractionation curve for the aromatic hydrocarbons of the octane catalyzate.
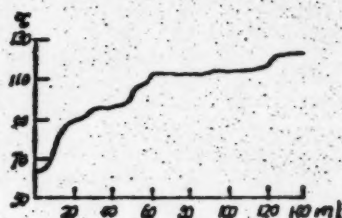
Fig. 4. Fractionation curve for the paraffin part of the octane catalyzate.

For Raman-spectrum investigation the united Fractions I and II, the united Fractions V and VI, and Fraction III were taken. The analysis showed that Fractions I + II contained about 60% of 2-methylpentane, 20% of hexane, and a certain amount of 2,2-dimethylpentane (detected qualitatively). Fraction III consisted mainly of heptane. Fraction IV, being a transitional one, was not investigated. Fractions V + VI consisted approximately of 70% of 2,4-dimethylhexane and 30% of 2,3-dimethylhexane.

According to their properties, Fraction VII contained mainly 2,3-dimethylhexane, Fraction VIII mainly 2-methylheptane, and Fraction IX mainly 4-methylheptane. The properties of Fraction X and of the residue indicated that they consisted mainly of unchanged octane.

It is of interest to compare the transformations of the alkanes investigated, and the material required for the comparison is presented in Table 6, from which it will be seen that, as the molecular weight of the alkane increases, the degree of conversion in the catalytic treatment rises; the amount of aromatic hydrocarbons formed also rises.

TABLE 5
Fractional Composition of the Paraffin Part of the Octane Catalyzate

Fraction No.	Boiling range (°C)	Amount(g)	n_D^{20}	d_4^{20}	Yield (%) on cataly-zate	Yield (%) on octane taken	Yield (%) on mixture of al-kanes taken for fractionation
I	57.0-86.5	10.2	1.3890	0.6813	6.3	4.1	10.0
II	86.5-89.0	6.5	1.3825	0.6857	3.9	2.5	5.1
III	89.0-98.5	8.3	1.3860	0.6890	5.0	3.2	8.1
IV	98.5-106.5	8.2	1.3930	0.6935	5.0	3.2	8.0
V	106.5-110.5	15.2	1.3990	0.6975	9.1	5.9	14.8
VI	110.5-115.5	16.0	1.3995	0.7126	9.5	6.2	15.7
VII	115.5-117.5	5.1	1.4010	0.7106	3.0	1.9	5.0
VIII	117.5-118.5	10.7	1.4020	0.7020	6.5	4.2	10.5
IX	118.5-125.0	2.1	1.3980	0.7025	1.2	0.8	2.0
X	125 -126.0	10.5	1.3980	0.7031	6.3	4.1	10.3
	Residue	8.4	1.3980	0.7033	5.0	3.2	8.3

TABLE 6
Nature of the Transformations of Hexane, Heptane, and Octane

| Transformation products (% on original alkane)	Alkane Hexane	Alkane Heptane	Alkane Octane
Degree of conversion (%)	69.8	84.4	92.7
Gaseous products	31.0	31.5	34.7
Liquid catalyzate	69.0	63.3	63.8
Aromatic hydrocarbons	4.8	12.3	21.0
Branched paraffins (isomeric to alkane)	31.4	37.9	23.9
those having a tertiary C	28.8	30.0	19.0
those having a quaternary C	1.5	6.7	3.2
branched paraffins not accounted for	1.1	1.2	1.7
Paraffins of lower molecular weight	2.6	2.7	13.0
2-methylbutane	1.2	1.4	1.5
pentane	1.4	1.3	1.7
hexane and its isomers	—	—	6.6
heptane and its isomers	—	—	3.2
Unchanged alkane	30.2	15.6	7.3
Losses	1.0	—	—

Isomerization of the alkanes leads mainly to the formation of hydrocarbons having a tertiary carbon atom. Together with isomers having only one side chain, however, an appreciable amount of more highly branched paraffins is formed.

An examination of the chemical nature of the octane catalyzate gives us reason to suppose that, under the given conditions, the nature of the contact-catalysis reactions of this alkane is quite analogous to that of the various transformations of its homologs, heptane and hexane. In this case also, the reactions of dehydrocyclization, alkylation, isomerization, and hydrogenolysis are clearly manifest. The properties of the residue from the fractionation of the aromatic hydrocarbons formed (benzene, toluene, and xylenes) show that it consists of higher benzene homologs, arising by the methylation of xylenes with methylene radicals:

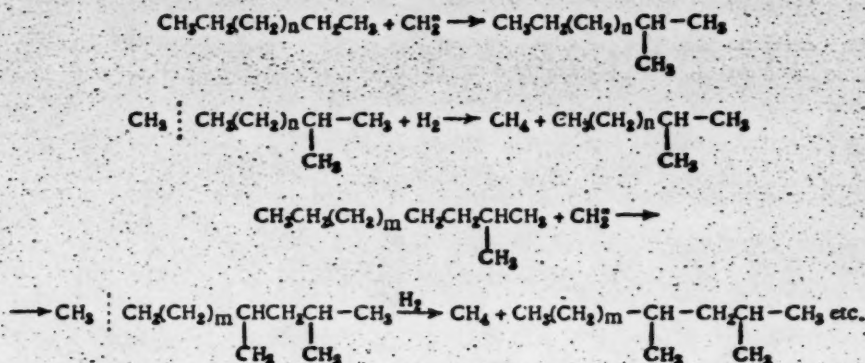$$C_6H_4(CH_3)_2 + CH_2 \longrightarrow C_6H_3(CH_3)_3 \ etc.$$
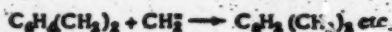
The question arises of the mechanism of the formation of the isomeric paraffins. It is evident that in the catalytic treatment of alkanes, as also in that of cycloalkanes, an important part is played in their transformations

by methylene breakdown of part of the substance, with subsequent methylation of alkanes by the methylene radicals formed, yielding branched hydrocarbons, e.g.:

$$CH_3CH_2CH_2CH_2CH_3 + CH_2^{\cdot} \longrightarrow CH_3CH-CH_2CH_2CH_3 \text{ etc.}$$
$$\underset{CH_3}{|}$$
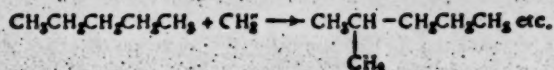
This concept of ours on the ways in which branched paraffins are formed under the conditions of the contact-catalysis reactions of normal alkanes at high temperatures and at high pressures of hydrogen is based, as we have seen, on the synthetic process of alkylation by means of radicals; we are inclined to make this same concept the basis of our explanation of the mechanism of the isomerization of n-alkanes under these conditions, our scheme for the process, which consists of successive methylation and hydrogenolysis reactions, being as follows:

$$CH_3CH_2(CH_2)_nCH_2CH_3 + CH_2^{\cdot} \longrightarrow CH_3CH_2(CH_2)_n CH-CH_3$$
$$\underset{CH_3}{|}$$

$$CH_3 \vdots CH_2(CH_2)_nCH-CH_3 + H_2 \longrightarrow CH_4 + CH_3(CH_2)_nCH-CH_3$$
$$\underset{CH_3}{|} \qquad \qquad \underset{CH_3}{|}$$

$$CH_3CH_2(CH_2)_m CH_2CH_2CHCH_3 + CH_2^{\cdot} \longrightarrow$$
$$\underset{CH_3}{|}$$

$$\longrightarrow CH_3 \vdots CH_2(CH_2)_m CHCH_2CH-CH_3 \xrightarrow{H_2} CH_4 + CH_3(CH_2)_m-CH-CH_2CH-CH_3 \text{ etc.}$$
$$\underset{CH_3}{|} \underset{CH_3}{|} \qquad \qquad \underset{CH_3}{|} \underset{CH_3}{|}$$

SUMMARY

1. A study has been made of the contact-catalysis reactions of hexane, heptane, and octane in presence of platinized alumina at 460° under a high pressure of hydrogen (15-20 atm).

2. It has been shown that in all cases, under the given conditions, dehydrocyclization and isomerization of the alkanes occur, and both the alkanes themselves, and also benzene homologs formed as a result of catalytic dehydrocyclization, undergo methylation and hydrogenolysis.

3. It has been suggested that the methylene breakdown of alkanes and cycloalkanes plays a part in the formation of branched paraffins and higher benzene homologs.

4. A new concept has been advanced relating to the contact-catalysis isomerization reactions of alkanes at high temperatures in presence of hydrogen at high pressure.

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[1] N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 2, 271 (1953).

[2] B. L. Moldavsky, G. L. Kanusher, and M. V. Kobylskaya, J. Gen. Chem., 7, 167 (1937).

SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XVII. PREPARATION OF α,β-UNSATURATED CYCLIC KETONES (2-CYCLOALKEN-1-ONES)

I. N. Nazarov, L. D. Bergelson, I. V. Torgov, and S. N. Ananchenko

In a series of communications [1] we have described numerous condensations of dienes with α,β-unsaturated cyclic ketones leading to the synthesis of various polycyclic compounds, including compounds related to steroids.

Among the unsaturated cyclic ketones employed in these condensations were: 2,4-dimethyl-2-cyclopenten-1-one (I), 2-methyl-2-cyclohexen-1-one (II), 2-methyl-2-cyclopenten-1-one (III), 2-cyclohexen-1-one (IV), and 2-cyclopenten-1-one (V).
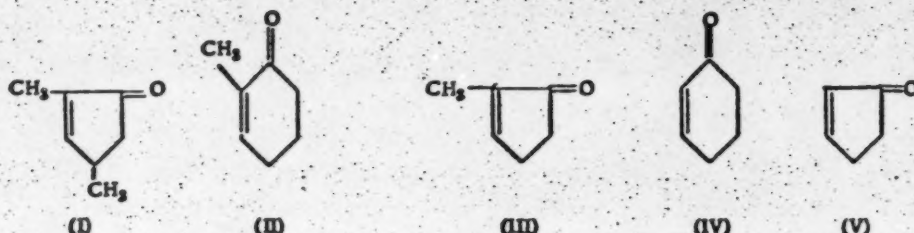
Although 2,4-dimethyl-2-cyclopenten-1-one (I) is simply prepared by the method discovered in our laboratory [2], which is based on the cyclization of allyl vinyl ketones, the preparation of the ketones II, III, IV, and V presents considerable difficulties.

A review of the literature shows that no satisfactory method for the synthesis of α,β-unsaturated cyclic ketones exists, all the methods described for their preparation being complicated and giving poor yields.

Certain α,β-unsaturated ketones have been prepared by Koetz [3] from α-bromo or α-chloro ketones, with elimination of hydrogen bromide or chloride:
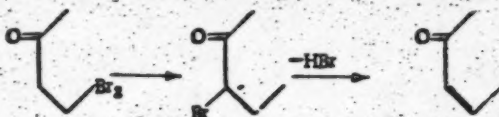
In spite of the commonplace character of this method, it has been studied rather superficially and has given very low yields of unsaturated ketones (5-8%). In the case of 2-cyclohexen-1-one, Koetz gives no indication at all of the yield.
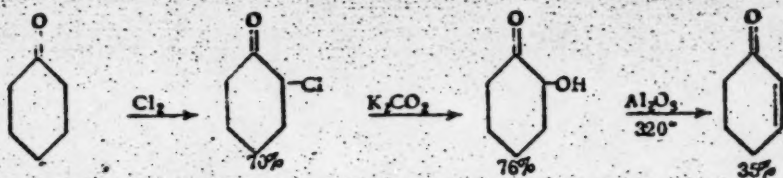
An interesting method for the preparation of cyclohexenones has been proposed by Birch [4] who reduced phenol ethers and aromatic amines with sodium and alcohol in liquid ammonia:
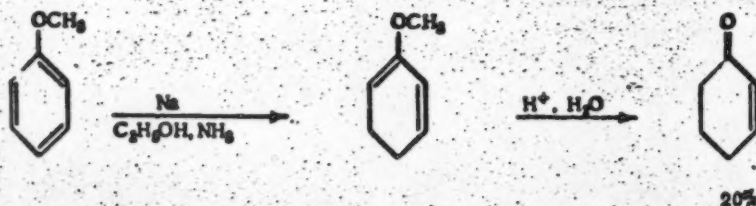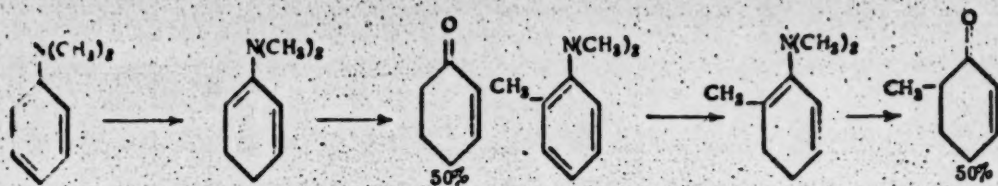
In all cases, however, the products included isomers having the double bond in another (non-conjugated) position, and this made the purification of the 2-cyclohexen-1-ones very difficult. This method is quite unsuitable for the preparation of 2-methyl-2-cyclohexen-1-one.

A relatively satisfactory method for the preparation of 2-cyclohexen-1-one was developed by Bartlett and Woods [5]:
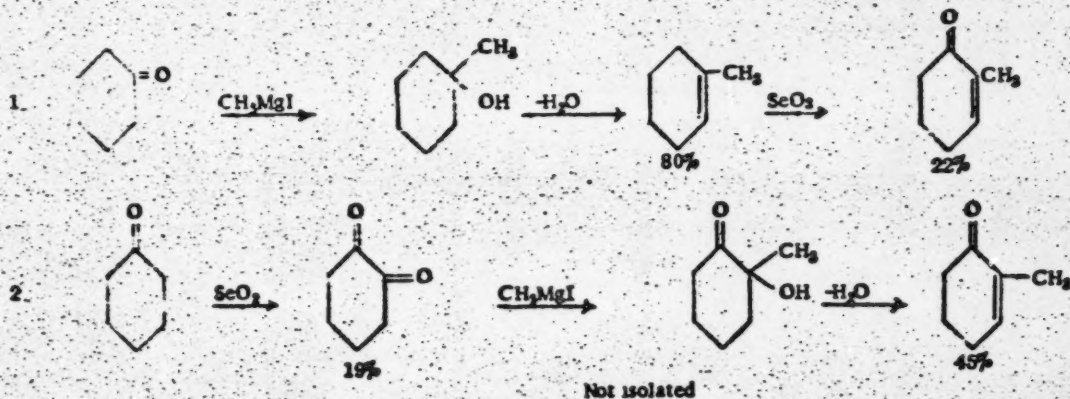

The overall yield was 18%.

An original method has been proposed also by Rigby [6], who started from the more expensive resorcinol:
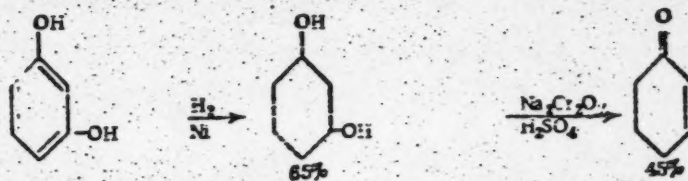
The overall yield was 29%.
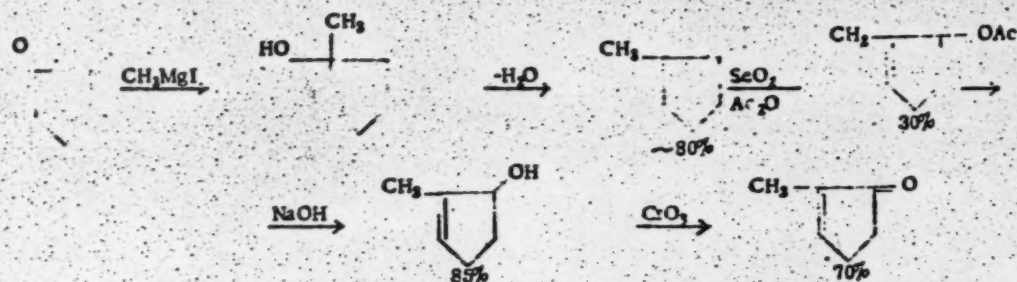
Up to now no satisfactory method for the preparation of 2-methyl-2-cyclohexen-1-one has been given. Thus [...] obtained it by the following two methods:

1.

2.

Not isolated

The first method gave an overall yield of 18%, but after fractionation and purification analysis gave a low (by 2%) carbon content. The second method gave an overall yield of 9% of ketone, which again was not pure.

It is interesting to note that the method of brominating 2-methylcyclohexanone and then eliminating hydrogen bromide was not used, because Koetz has asserted [8] that the bromine attacks the unsubstituted methylene group, so that elimination of hydrogen bromide yields not 2-methyl- but 6-methyl-2-cyclohexen-1-one. As will be shown below, this assertion is incorrect, and the bromination of 2-methylcyclohexanone, as that of other 2-methyl-cycloalkanones, occurs only at the tertiary carbon atom. It was on account of the same preconceived idea that Mousseron [9], without any proof, ascribed the structure of 2-chloro-5-methylcyclopentanone to the chlorination product of 2-methylcyclopentanone.

2-Methyl-2-cyclopenten-1-one (III) was synthesized by Dane [10] as follows:

$$CH_3MgI \quad HO\!-\!CH_3 \quad \xrightarrow{-H_2O} \quad CH_3 \quad \xrightarrow[Ac_2O]{SeO_2} \quad \sim 80\% \quad CH_2\!-\!OAc \quad 30\%$$

$$\xrightarrow{NaOH} \quad CH_3 \; OH \quad 85\% \quad \xrightarrow{CrO_3} \quad CH_3\!-\!O \quad 70\%$$

The yield was about 14% on the amount of cyclopentanone taken.

A simpler method was proposed by Rinkes [11]:

$$CH_3 \quad \xrightarrow{C_2H_5ONO} \quad CH_2\!=\!NOCl \quad 70\% \quad \xrightarrow[H_2SO_4]{AcONa} \quad CH_3\!-\!O \quad 62\%$$
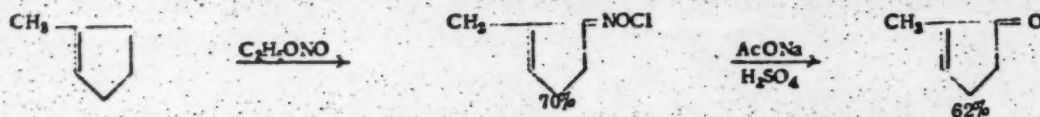
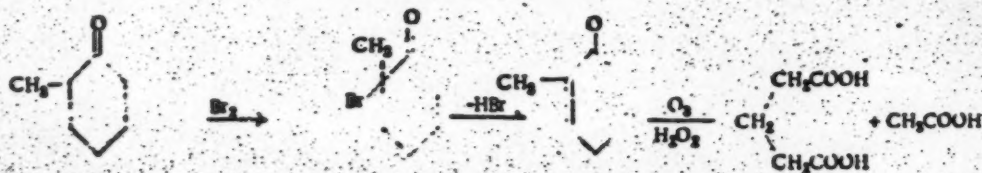In this method the yield was 33% on the amount of cyclopentanone taken.

2-Cyclopenten-1-one (V) was prepared by Dane [12] in a similar manner, the overall yield being less than 5% on the amount of cyclopentene taken.

We have here cited methods that are the most acceptable with respect to the ultimate yield, and have omitted other syntheses, in which a,β-unsaturated cyclic ketones are obtained in insignificant yield [12, 14].

In this paper we give a general method for the preparation of a,β-unsaturated cyclic ketones: it is based on the bromination of saturated cyclic ketones and subsequent elimination of hydrogen bromide. We give also a simplified method for the preparation of 2,4-dimethyl-2-cyclopenten-1-one.

The bromination of 2-methylcyclohexanone was performed in an irradiated water-chloroform system at 30-35° in presence of calcium carbonate. At a lower temperature the reaction proceeds irregularly, and the yield is lower. Bromination by means of dioxane dibromide in ether gives worse results.

In the early experiments the bromo ketone was isolated by vacuum distillation, but it was later found to be more expedient to treat it immediately, without isolation, with diethylaniline. The elimination of hydrogen bromide was carried out at 100°, and the 2-methyl-2-cyclohexen-1-one formed was distilled off (58% yield). As the results of ozonization showed, none of the isomeric 6-methyl-2-cyclohexen-1-one was formed: only acetic and glutaric acids were isolated after ozonization; no methylglutaric acid was detected:

$$CH_3 \xrightarrow{Br_2} \quad CH_3 \; Br \xrightarrow{-HBr} \quad CH_3 \xrightarrow[H_2O_2]{O_3} \quad CH_2\!-\!CH_2COOH \;/\; CH_2COOH \; + \; CH_3COOH$$

It has thus been proved beyond doubt that the bromination of 2-methylcyclohexanone occurs entirely at the tertiary carbon atom; this is in complete accord with A. E. Favorsky's results [15] on the bromination of 3-methyl-2-butanol, in which the bromine again reacts at the tertiary carbon atom:

$$CH_3-CO-CH\diagdown{CH_3 \atop CH_3} \xrightarrow{Br_2} CH_3-CO-CBr\diagdown{CH_3 \atop CH_3}$$

Before beginning work on the development of a method for the preparation of 2-methyl-2-cyclopenten-1-one (III), we made an investigation in order to find the best method of preparing the 2-methylcyclopentanone required as starting material. We investigated the methylation of the sodium derivative of cyclopentanone with methyl iodide or dimethyl sulfate in ether or liquid ammonia at −76°. In the literature there is a description of the methylation of cyclopentanone with methyl iodide in presence of sodamide [16], but side reactions occurred leading to the formation of cyclopentylidenecyclopentanone (up to 90%) and products of the further methylation of methylcyclopentanone. We obtained a smaller amount of condensation products (40-50%), but in all of the experiments the methylation productconsisted of a mixture of cyclopentanone with mono- and di-methylcyclopentanones, the separation of which, owing to the closeness of the boiling points, was extremely difficult.

It was of interest to examine the use of the readily available 2-methylcyclohexanol for the preparation of 2-methylcyclopentanone. By oxidation of this it should be possible to obtain 2-methylhexanedioic acid (together with adipic acid), cyclization of which should yield the required ketone. Actually, oxidation of 2-methylcyclohexanol with nitric acid in presence of ammonium vanadate gave 2-methylhexanedioic acid in 70% yield. The cyclization of this, however, with the aid of baryta or acetic anhydride gave only 10-12% of 2-methylcyclopentanone. We therefore considered it more expedient to proceed by the usual method: the Dieckmann condensation of diethyl adipate, followed by methylation and decarboxylation [17]:
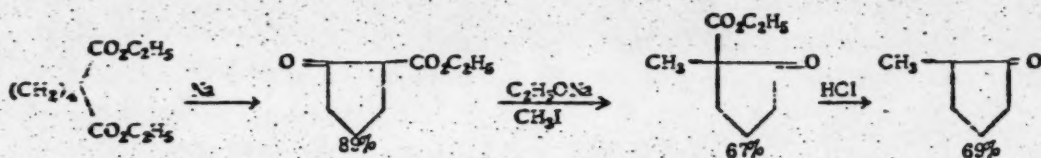
Although an excess of methyl iodide was used at the methylation stage, the ethyl ester of 1-methyl-2-oxocyclopentanecarboxylic acid was contaminated by the original 2-oxocyclopentanecarboxylic ester, which was removed by agitation of the product with cold caustic potash solution.

Bromination of 2-methylcyclopentanone was carried out in a water-chloroform system at 22-24° in presence of magnesium carbonate (calcium carbonate gave a lower yield). It was found that, when bromination was slow, addition of a few drops of hydrochloric acid was useful. Elimination of hydrogen bromide was effected with the aid of diethylamine, as in the case of 2-methylcyclohexanone. The yield of 2-methyl-2-cyclopenten-1-one (III) was 50% (on the 2-methylcyclopentanone that reacted).

As in the case of 2-methylcyclohexanone, bromination of 2-methylcyclopentanone occurs at the tertiary carbon atom, as the results of the ozonization of the methylcyclopentanone showed. Only succinic and acetic acids were obtained, no methylsuccinic acid being detected:
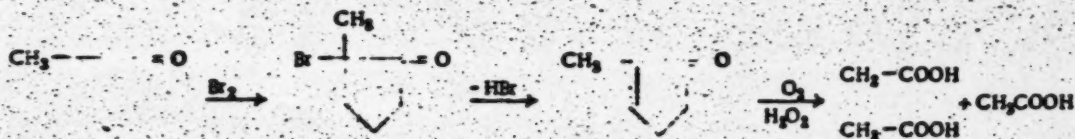
Bromination of cyclohexanone, unlike that of the two ketones already discussed, proceeds with some difficulty. It was found, however, that it could be carried out smoothly by adding about 20% of cyclohexanol to the cyclohexanone and increasing the amount of bromine correspondingly. The elimination of hydrogen bromide from 2-bromocyclohexanone required a higher temperature (about 150°). The yield of 2-cyclohexen-1-one (IV)

was 35% (on the cyclohexanone that reacted).

2-Cyclopenten-1-one (V) was prepared in a precisely similar manner by bromination of cyclopentanone followed by elimination of hydrogen bromide from the 2-bromocyclopentanone formed, but as a result of resinification the yield was only 25% (on the cyclopentanone that reacted).

Ozonization of 2-cyclohexen-1-one and 2-cyclopenten-1-one yielded glutaric and succinic acids respectively:
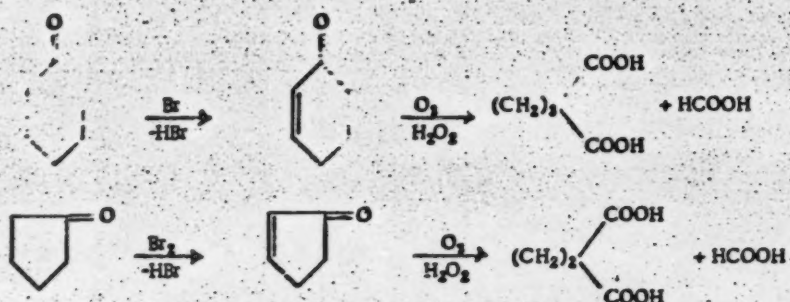

Details concerning the α,β-unsaturated cyclic ketones that we have prepared are given in the table.

TABLE

Name of ketone	B.p. (°C/ mm)	n_D^{20}	M.p. of semicarbazone (°C)	
			our results	data in lit.
2-Methyl-2-cyclohexen-1-one	56/ 9	1.4865	206-207 (dec.)	208 [14]
2-Methyl-2-cyclopenten-1-one	52-53/ 15	1.4770	218 (dec.)	220 (dec.) [10]
2-Cyclohexen-1-one	63.5/ 23	1.4872	161	160 [3]
2-Cyclopenten-1-one	45/ 12	1.4720	214-215	214 [12]

We have also simplified the method for the preparation of 2,4-dimethyl-2-cyclopenten-1-one (I). It has been prepared previously from 2-methyl-1,5-hexadien-3-yne in three stages:
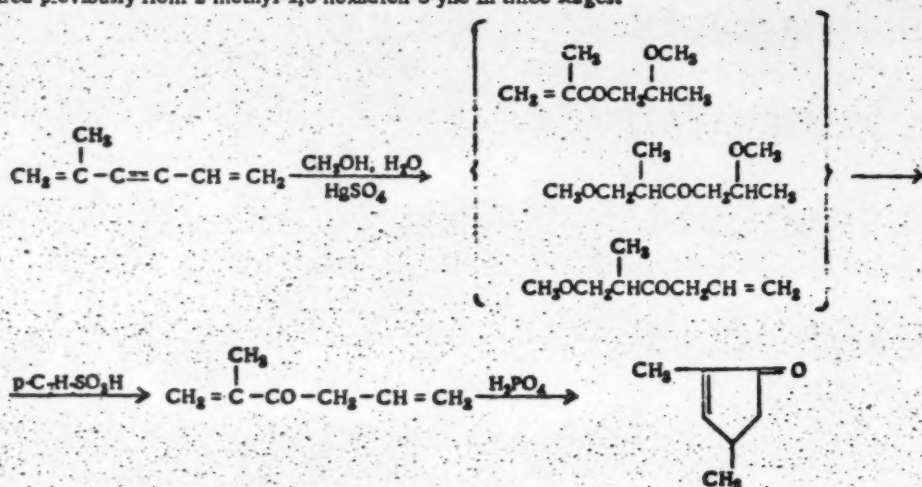
It was found that the stage in which methanol is eliminated from the methoxy ketones could be omitted, the latter being subjected directly to the treatment with acid (phosphoric or hydrochloric). In this way not only was the overall yield of the dimethylcyclopentanone I increased (by about 40%), but the time required for the preparation was greatly reduced.

EXPERIMENTAL

2-Methylcyclohexanol

A mixture of 500 g of o-cresol (m.p. 190-193°; n_D^{20} 1.545), 20 ml of alcohol, and 15 g of Raney nickel was placed in a two-liter rotating autoclave. Hydrogen at a pressure of 120 atm was introduced from a cylinder, and the autoclave was heated to 120°. After 2 hours 30 minutes the pressure had fallen almost to zero. More hydrogen was passed in under a pressure of 120 atm, and the temperature was raised to 160-170°. After two hours the pressure had fallen to 75 atm and hydrogenation had ceased (the pressure of hydrogen remained constant at a given temperature). The autoclave was rotated for a further two hours at 170°, cooled, and discharged. The contents were filtered, and the filtrate was vacuum-fractionated, yielding:

Fraction I, b.p. 66-78° at 29 mm; 11 g; n_D^{20} 1.4590
Fraction II, b.p. 78-80° at 29 mm; 487 g; n_D^{20} 1.4610

Residue 3 g

Fraction II was 2-methylcyclohexanol; yield 92%.

2-Methylcyclohexanone

A mixture of 350 g of 2-methylcyclohexanol (b.p. 78-80° at 29 mm; n_D^{20} 1.4610) and 250 ml of ether was placed in a three-liter flask fitted with mechanical stirrer, dropping funnel, and thermometer. An oxidizing mixture prepared by dissolving 350 g of sodium dichromate dihydrate and 455 g of sulfuric acid in 1500 ml of water was then added over a period of six hours with vigorous stirring and cooling (a temperature of −3 to −7° was maintained). The reaction mixture was stirred for one hour at −2°, placed in ice overnight, and stirred on the next day for three hours at 0°. The ether layer was separated, and the water layer was extracted four times with ether. The united ether extracts were shaken with potassium carbonate until neutralized, and then dried with magnesium sulfate. The ether was distilled off, and the residue was vacuum-distilled, yielding 296 g (87%) of 2-methylcyclohexanone, b.p. 51-52° at 13 mm; n_D^{19} 1.4482.

2-Methyl-2-cyclohexen-1-one (II)

A mixture of 224 g (2 moles) of 2-methylcyclohexanone, 220 ml of water, and 112 g of finely ground calcium carbonate was placed in a two-liter flask fitted with mechanical stirrer, dropping funnel, and thermometer. The mixture was vigorously stirred for 30 minutes while irradiated with a 1000-watt lamp, and, with the temperature at 30°, addition of a solution of 320 g (2 moles) of bromine in 260 ml of chloroform was begun.

Bromination began immediately, and addition of bromine was continued for 30-40 minutes, the temperature being maintained in the range 30-35°. When reaction was complete, the upper layer was separated and the water layer was extracted three times with ether. The ether-chloroform extract was washed with a solution of sodium bicarbonate and sodium thiosulfate, and then 320 ml (2.15 moles) of diethylaniline was added. The solution was dried with sodium sulfate, and the solvents were slowly removed at a moderately low pressure over a period of 5-6 hours. The contents of the flask were then heated for three hours in a boiling water bath, the pressure being gradually lowered to 20-25 mm, and a mixture of 2-methyl-2-cyclohexen-1-one, 2-methylcyclohexanone, and diethylaniline gradually came over; toward the end the pressure was reduced to 7-10 mm. The distillate (173 g; n_D^{20} 1.4840) was fractionated through a Fenske column (5-6 theoretical plates) having a glass filling. The fractions obtained were:

Fraction I, b.p. 43-44° at 8 mm; 20 g; n_D^{20} 1.4550
Fraction II, b.p. 44-54° at 9 mm; 19 g; n_D^{20} 1.4720
Fraction III, b.p. 54-56° at 9 mm; 10 g; n_D^{20} 1.4835
Fraction IV, b.p. 56° at 9 mm; 108 g; n_D^{20} 1.4865

Residue 14 g

Fraction I was unchanged 2-methylcyclohexanone. Fraction III contained more than 90% of the methylcyclohexenone II. Fraction IV was pure 2-methyl-2-cyclohexen-1-one (II), b.p. 56° at 9 mm; n_D^{20} 1.4865; d_4^{20} 0.9667. The overall yield was 58% (on the amount of methylcyclohexanone that reacted). In this way we prepared more than 3 kg of 2-methyl-2-cyclohexen-1-one. The semicarbazone melted at 206-207°.

Ozonization of 2-Methyl-2-cyclohexen-1-one (II)

Ozonized oxygen (5% ozone) was passed at 0° for ten hours at 6-7 liters per hour through a solution of 6.8 g of the substance II in 35 ml of chloroform. Water (50 ml) and 30% hydrogen peroxide (5 ml) were added to the

ozonide solution, which was then stirred at 50° for three hours. The mixture was cooled and neutralized with sodium carbonate, and the aqueous solution was separated and evaporated to dryness under reduced pressure. The dry salts were dissolved in 18 ml of 30% hydrochloric acid, and the organic acids were extracted by several treatments with ether. The ether solution was dried with magnesium sulfate, and, after removal of ether, volatile acids were distilled off at moderately low pressure. The product was 2.35 g of acetic acid, which was identified by the carodyl test, absence of formic acid being proved by the calomel method. The residue after removal of volatile acids was vacuum distilled, and yielded 4.8 g of glutaric acid, b.p. 165°/4 mm, which completely solidified (m.p. 96°). In admixture with authentic glutaric acid there was no melting point depression.

Bromination of 2-Methylcyclohexanone with Dioxane Dibromide

Dioxane dibromide was prepared by Favorsky's method [18]. Dry dioxane (b.p. 100-101°; 53 g, i.e., 0.6 mole) was placed in a porcelain beaker and was constantly stirred with a glass rod while bromine (80 g, i.e., 0.5 mole) was added gradually in small portions. The reaction mixture was heated to 60-70° and then cooled, when it solidified to an orange crystalline mass, which was dried in the air between two sheets of filter paper. A theoretical yield (125 g) of dioxane dibromide was obtained.

A mixture of 100 ml of absolute ether and 56 g (0.5 mole) of 2-methylcyclohexanone was placed in an Erlenmeyer flask and was stirred for two hours while dioxane dibromide (125 g, i.e., 0.5 mole) was added in small portions, the temperature being maintained at not above 22-23°. There was a vigorous evolution of hydrogen bromide. When the addition was complete, the reaction mixture was washed with 10% caustic soda solution until neutral, and then with a saturated solution of sodium thiosulfate. The ether layer was separated and mixed with 75 g (0.5 mole) of diethylaniline. Elimination of hydrogen bromide and isolation of the ketone II were performed by the method described in the preceding experiment. The products were 3 g of unchanged methylcyclohexanone and 21.5 g of 2-methyl 2-cyclohexen-1-one, b.p. 61-63° at 14 mm; n_D^{20} 1.4845; the yield was 47% (on the amount of methylcyclohexanone that reacted). When the bromination was performed under the same conditions, but with an addition of calcium carbonate, practically the same results were obtained.

Methylation of Cyclopentanone

Sodamide was prepared by Neuwland's method [19]. Liquid ammonia (250 ml), sodium (1.5 g), and ferric nitrate (0.15 g) were placed in a three-necked one-liter flask fitted with mercury-sealed stirrer, thermometer, dropping funnel, and tube for passage of air. The flask was cooled with dry ice, and dry air was passed through the mixture until a colorless solution was obtained. More sodium (10 g) was then added, and the mixture was stirred until the blue color disappeared. Absolute ether (200 ml) was added, the cooling mixture was removed, and the ammonia was allowed to evaporate at room temperature. When the temperature in the flask had become equal to that of the room, the mixture was again cooled to −70° and was stirred vigorously while 42 g (0.5 mole) of cyclopentanone was added over a period of five minutes; the temperature rose to −50°. Then, over a period of five minutes, 85 g (0.59 mole) of methyl iodide was added, and the temperature rose to 15°, in spite of the applied cooling with dry ice. The mixture was stirred for a further ten minutes and then decomposed by addition of 40 g of dry ammonium chloride, which was followed by 250 ml of water. The usual treatment and vacuum distillation yielded 20 g of distillate, b.p. 30-40°/15 mm, and 11 g, b.p. 125-129°/9 mm.

Fractionation of the first portion of the distillate under ordinary pressure gave the following fractions:

Fraction I, b.p. 80-132°; 1 g; n_D^{20} 1.4390
Fraction II, b.p. 132-136°; 12 g; n_D^{20} 1.4360
Fraction III, b.p. 136-139°; 6 g; n_D^{20} 1.4360

The semicarbazone obtained from Fraction II melted at 175-184°, thus indicating that the fraction was a mixture of various methylation products of cyclopentanone (m.p. of semicarbazones: methylcyclopentanone 170-171°, dimethylcyclopentanone 191° [20]).

Methylation of the sodium derivatives of cyclopentanone in liquid ammonia with methyl iodide and dimethyl sulfate again gave a mixture of products, including, moreover, a considerably greater proportion of highboiling condensation products.

Oxidation of 2-Methylcyclohexanol

Nitric acid of sp.gr. 1.4 (245 ml) was placed in a three-necked one-liter flask fitted with mechanical stirrer, thermometer, dropping funnel, and reflux condenser. The acid was heated to 108°, and additions were made of 0.25 g of ammonium vanadate and a few drops of 2-methylcyclohexanol; oxides of nitrogen were evolved. The reaction mixture was cooled to 80°, and 50 g of 2-methylcyclohexanol was added at 60-70° over a period of one hour. The mixture was then heated in a water bath for one hour, and was placed in an ice bath overnight.

On the next day the precipitated crystals (9 g) were filtered off under suction; they melted at 108-115° and consisted mainly of adipic acid.

The filtrate was evaporated to dryness, and the viscous oil that remained solidified (m.p. 54-73°). It was dissolved in 200 ml of ether and set aside at 0° overnight. A further 3 g of adipic acid, m.p. 120-128° was precipitated. The greater part of the ether was removed under reduced pressure, and 50 g of crystals, m.p. 60-67°, was precipitated; they consisted essentially of 2-methylhexanedioic acid (published values for the melting point of 2-methylhexanedioic acid range from 57° to 64° [21]).

Cyclization of 2-Methylhexanedioic Acid

A mixture of 42 g of 2 methylhexanedioic acid, prepared as above, and 2.1 g of barium hydroxide was placed in a Wurtz flask, which was then heated on a Babo funnel. Distillation began at 285-295°, and was continued for two hours. The ketone was salted out of the distillate with potassium carbonate, and was extracted with several portions of ether. The usual treatment and fractionation yielded:

Fraction I. b.p. 125-135°; 0.5 g; n_D^{20} 1.4362.
Fraction II. b.p. 135-136°; 3.0 g; n_D^{20} 1.4365.
Residue 0.5 g.

The yield was, therefore, 12%.

The semicarbazone prepared from Fraction II melted at 170-171°, and the melting point was not depressed by addition of the semicarbazone of 2 methylcyclopentanone. Cyclization by Blanc's method [22] by the use of acetic anhydride, gave 10% of ketone.

Preparation of Diethyl Adipate

A mixture of 1000 ml of benzene, 600 ml of alcohol, 400 g of adipic acid, and 100 ml of concentrated sulfuric acid was placed in a three liter flask fitted with mechanical stirrer and reflux condenser. The mixture was boiled and stirred vigorously for five hours. The benzene layer was separated, and the aqueous layer was extracted twice with benzene. The mixture of water, alcohol, and benzene was distilled off under a moderately low pressure. Distillation of the residue yielded 539 g (97%) of diethyl adipate, b.p. 127-128°/13 mm, n_D^{21} 1.4280.

Preparation of the Ethyl Ester of 2-Oxocyclopentanecarboxylic Acid

A mixture of 49.5 g(2.15 moles) of "molecular" sodium (all the sodium must be in a finely dispersed condition) in 1260 ml of absolute toluene, 303 g (1.5 moles) of diethyl adipate, and 15 ml of absolute alcohol was vigorously stirred while being heated under reflux in a water bath in a three necked three-liter flask. The sodium derivatives began to come down at 60-70°. The mixture was heated for four hours in the boiling water bath, and the whole mass finally solidified and was set aside overnight. On the next day 200 ml of toluene was added, and the mixture was decomposed with 700 ml of 7% HCl. The toluene layer was separated, and the water layer was extracted with toluene. The united extracts were washed with water and dried with magnesium sulfate. Toluene was removed under reduced pressure, and the residue was distilled, yielding 209 g (89%) of the ethyl ester of 2-oxocyclopentanecarboxylic acid, b.p. 110-113°/22 mm, n_D^{21} 1.4525.

Methylation of the Ethyl Ester of 2-Oxocyclopentanecarboxylic Acid

Sodium ethoxide was prepared by dissolving 44.2 g (1.92 g-atoms) of sodium in 1000 ml of absolute alcohol contained in a three-necked three-liter flask fitted with mechanical stirrer, dropping funnel, and reflux condenser. The ethoxide solution was cooled to −13° and was stirred while 300 g (1.92 moles) of the ethyl ester of 2-oxocyclopentanecarboxylic acid, cooled to −13° to −15°, was added over a period of 30 minutes. While stirring was being continued at the same temperature, 275 g (1.97 moles) of methyl iodide was added in one lot, and stirring was further continued while the temperature was raised to that of the room, which took 5-6 hours: during this time the voluminous precipitate of sodium derivative gradually disappeared. The reaction mixture was set aside at room temperature overnight, and on the next day the greater part of the alcohol was distilled off under reduced pressure. The residue was treated with 200 ml of water and carefully extracted with ether. The extract was dried with sodium sulfate, the ether was removed, and the residue gave 286 g of distillate, b.p. 106-118°/16 mm, n_D^{20} 1.4465. The distillate gave an intense violet color with alcoholic ferric chloride.

Purification of the product from unchanged 2-oxocyclopentanecarboxylic ester was effected by introducing it into a two-liter flask fitted with mechanical stirrer, adding 80 ml of ether, cooling to 0°, and adding

rapidly with vigorous stirring a solution, also cooled to 0°, of 32 g of caustic potash in 800 ml of water. Stirring was continued for three minutes. The ether layer was separated, and the water layer was extracted with ether. The ether extracts were dried with calcium chloride, and the solvent was distilled off. Fractionation of the residue yielded 224 g (67%) of the ethyl ester of 1-methyl-2-oxocyclopentanecarboxylic acid, b.p. 116–119°/25 mm, n_D^{20} 1.4465. The product gave no color with ferric chloride.

Preparation of 2-Methylcyclopentanone

A mixture of 510 ml of concentrated hydrochloric acid, 1020 ml of water, and 255 g of the ethyl ester of 1-methyl 2-oxocyclopentanecarboxylic acid was placed in a three-necked three-liter flask fitted with mercury-sealed stirrer and reflux condenser; the latter was fitted with a delivery tube that passed to a flask containing ether for the absorption of methylcyclopentanone vapor carried away by carbon dioxide evolved. The stirred mixture was heated in a water bath for nine hours. During the first two hours there was vigorous evolution of carbon dioxide, which then subsided. The solution was cooled and carefully extracted with ether (ten times). The ether extracts (together with the ether from the absorption vessel) were washed with a concentrated solution of sodium carbonate, and then dried with calcium chloride. The solution was transferred to a flask fitted with a large Vigreux column, and the ether was distilled off and the residue fractionated, 98 g (69%) of a fraction of b.p. 136–137°, n_D^{20} 1.4360, being collected. This was 2-methylcyclopentanone; the semicarbazone melted at 170–171°. Altogether, 700 g of methylcyclopentanone was obtained by this method. When alkaline hydrolysis was used, the yield of methylcyclopentanone fell to 50–54%.

Preparation of 2-Methyl-2-cyclopenten-1-one (III)

A mixture of 98 g (1 mole) of 2-methylcyclopentanone, 50 ml of chloroform, 62 g of magnesium carbonate, and 150 ml of water was placed in a three-necked 500-ml flask fitted with mechanical stirrer, dropping funnel, and thermometer. The suspension was stirred at 22–24° for two hours while 152 g (0.95 mole) of bromine was added. In order to initiate the reaction it is useful to add 0.5–1 ml of concentrated hydrochloric acid while the stirrer is stopped; this creates a local concentration of hydrogen ions, which promote reaction. When all of the bromine had been added, the chloroform layer was separated and the water layer was extracted three times with ether. To the combined extracts 160 ml (1.07 moles) of diethylaniline was added, and the solution was dried with sodium sulfate. The solvents were distilled off under a moderately low pressure, and, with the pressure reduced to 25 mm, the residue was heated in a boiling water bath, when a mixture of methylcyclopentanone, 2-methyl-2-cyclopenten-1-one, and diethylaniline passed over to the receiver, which was cooled in a freezing mixture. The distillate (67 g) was fractionated through a Fenske column having a glass filling:

Fraction I   b.p. 37–39° at 15 mm;   17 g; n_D^{21} 1.4360
Fraction II   b.p. 39–52° at 15 mm;   2 g; n_D^{22} 1.4430
Fraction III b.p. 52–53° at 15 mm;   40 g; n_D^{20} 1.4770
Residue 4 g.
Fraction I was almost pure 2-methylcyclopentanone, and Fraction III was pure 2-methyl-2-cyclopenten-1-one. The yield was therefore 51% (on the amount of methylcyclopentanone that reacted).

The semicarbazone melted at 128° (decomposition; in a sealed capillary), and the oxime at 122° (from alcohol). Dane [10] gives 220° (decomposition) and 128° respectively.

Replacement of magnesium carbonate with calcium carbonate lowered the yield to 40%. Replacement of chloroform with carbon tetrachloride lowered the yield still more.

Ozonization of 2-Methyl-2-cyclopenten-1-one (III)

A solution of 2.0 g of 2-methyl-2-cyclopenten-1-one in 30 ml of chloroform was ozonized at 0°, 18 liters of ozonized oxygen (6% ozone) being passed in the course of 4 hr, 30 min. Water (10 ml) and 30% hydrogen peroxide (6 ml) were added to the chloroform solution of the ozonide. The mixture was heated with stirring at 60° for five hours, and then cooled. Sodium carbonate was added until carbon dioxide was no longer evolved (3.5 g altogether), and the water layer was separated, extracted with ether, and acidified with concentrated hydrochloric acid until it was strongly acid to Congo red (5 ml required). On cooling, the solution yielded crystals of acid, which were filtered off under suction and washed with a small amount of cold water. The product, after drying over phosphoric anhydride, was 1.05 g of succinic acid, m.p. 180–181°. A mixture melting point with authentic material showed no depression. The aqueous solution was extracted with benzene, and evaporation of the benzene under reduced pressure yielded a further 0.2 g of less pure succinic acid, m.p. 163–167°. The mother liquor gave a positive cacodyl reaction.

Preparation of 2-Cyclohexen-1-one (IV)

A mixture of 20 g of cyclohexanol, 80 g of cyclohexanone, and 70 g of calcium carbonate (chalk) was placed in a three-necked 500-ml flask fitted with stirrer, dropping funnel, and thermometer, and was warmed to 35°. To the stirred mixture, 192 g of bromine was added over a period of 4-4.5 hours, the temperature being maintained at 35-37° by regulation of the rate of addition of bromine. It was found that at first stirring must be slow, as otherwise the bromination is held back: in that case reaction may be promoted by stopping the stirrer and adding a few drops of cyclohexanol. The chalk must not be too finely ground, and a great excess must be avoided; otherwise, toward the end a difficultly separable emulsion is formed.

When all of the bromine had been added, stirring was continued for a further 30 minutes. The crude bromocompound was separated, and the water layer was extracted three times with ether. The ether extracts were added to the crude bromo compound, the solution was dried with magnesium sulfate, and the solvent was driven off under reduced pressure. It was found that the crude bromo compound had to be used quickly for the HBr-elimination reaction; otherwise it resinified. Also, it was necessary to take the bromo compound in small portions (20-50 g) for the HBr-elimination reaction; otherwise the reaction went with great difficulty and the yield of cyclohexenone fell.

Crude bromo compound (50 g) and diethylaniline (50 g) were placed in a Claisen flask having a Vigreux column. The elimination of hydrogen bromide was effected by rapid heating of the mixture at a residual pressure of 100 mm to 150-155°, 20 g of distillate being obtained. When all of the bromo compound had been treated in this way, the distillates were united and fractionated through a Fenske column having a glass filling; they yielded 20 g of unchanged cyclohexanone and 26 g (35% on the amount of cyclohexanone that reacted) of 2-cyclohexen-1-one, b.p. 63.5° at 23 mm, n_D^{20} 1.4872. The semicarbazone melted at 161° (from alcohol).

Preparation of 2-Cyclopenten-1-one (V)

A mixture of 45 g of cyclopentanone, 5 g of cyclopentanol, 100 ml of water, and 30 g of ground calcium carbonate (chalk) was placed in a three-necked 500-ml flask fitted with mechanical stirrer, dropping funnel, and thermometer. The mixture was warmed to 35°, and 80 g of bromine was added with stirring over a period of three hours. Treatment of the reaction mixture and the elimination of hydrogen bromide were carried out exactly as in the case of cyclohexanone. The yield of 2-cyclopenten-1-one, b.p. 45° at 12 mm, and n_D^{19} 1.4720 was 28%. The melting point of the semicarbazone was 214-215° (from alcohol).

Ozonization of 2-Cyclohexen-1-one (IV)

Ozonization was carried out as in the case of 2-methyl-2-cyclohexen-1-one, and 2.5 g of ketone yielded 1.7 g of glutaric acid, m.p. 97°. A mixture melting point with an authentic sample showed no depression.

Ozonization of 2-Cyclopenten-1-one (V)

Ozonization was carried out as in the case of 1-methyl-2-cyclopenten-1-one, and 4 g of ketone yielded 4.5 g of succinic acid, which melted after two crystallizations at 182-183°. A mixture melting point with an authentic sample showed no depression.

Preparation of 2,4-Dimethyl-2-cyclopenten-1-one (I)

1. Hydration of 2-Methyl-1,5-hexadien-3-yne. Water (180 ml) was placed in a five liter flask fitted with an efficient mechanical stirrer, and 11 g of sulfuric acid and 15 g of mercuric sulfate were dissolved successively in the water. Stirring was begun, and a solution of 800 g of 2-methyl-1,5-hexadien-3-yne in 1800 ml of methanol was added. The mixture was heated to 60°, and stirring was continued at that temperature for six hours, 1 g of finely ground mercuric sulfate being added after each hour. The mixture was set aside over night, and on the next day stirring was renewed and the temperature was brought to 60°; stirring continued for a further six hours, and 7 g of mercuric sulfate was added at the beginning and then 1 g per hour for the remaining time.

The liquid was transferred to a flask having a Vigreux column, and the bulk of the methanol was removed in a water bath at not above 35° under somewhat reduced pressure. The residue was neutralized to litmus with a solution of sodium methoxide (10 g of sodium in 200 ml of methanol), and 500 ml of ether and 50 g of zinc dust were added. The mixture was shaken vigorously and then allowed to stand for 4-5 hours with periodic shaking. The solution was filtered, 5-6 ml of dimethylaniline was added, and ether was removed in a water bath. Residual ether, methanol, and water were then removed under a moderately low pressure, and the residue was vacuum-distilled from a Claisen flask. Distillation was continued until, at a bath temperature of 130°, practically nothing further came over. The yield of methoxy ketone mixture, b.p. 70-100° at 20 mm was 900-960 g.

II. Cyclization of the Mixture of Methoxy Ketones with the Aid of Phosphoric Acid. The above described mixture of methoxy ketones (580 g) was placed in a three necked, two liter flask fitted with sealed mechanical stirrer, thermometer, and dropping funnel, and was stirred while 580 ml of phosphoric acid of sp.gr. 1.77 was added. The temperature gradually rose and attained 60-65° when about half of the acid had been added. Cooling was applied so that the temperature did not exceed 70°. Addition of acid occupied about one hour, and the reaction mixture was then heated at 70° for a further two hours. It was then cooled, 500 ml of water was added, and the mixture was stirred and cooled with water while 400 g of anhydrous sodium carbonate was added in small portions. The upper layer was separated, and the lower layer was extracted three times with ether (500 ml altogether). The combined extracts were neutralized with potassium carbonate powder (about 50 g), and then filtered. The ether was driven off, and the residue was distilled from a flask having a Vigreux column. Two fractionations yielded 300-325 g (49-53% on the amount of methylhexadienyne taken) of 2,4-dimethyl-2-cyclopenten-1-one, b.p. 61-62° at 16 mm, n_D^{20} 1.4675-1.4685.

III. Cyclization of the Mixture of Methoxy Ketones with the Aid of Hydrochloric Acid. A mixture of 1080 g of the above described mixture of methoxy ketones (b.p. 70-100° at 20 mm) and 2160 g of 18% hydrochloric acid was stirred for four hours at 80-85° in a three necked, five liter flask provided with sealed mechanical stirrer, thermometer, and dropping funnel. The mixture was then cooled and neutralized with sodium carbonate (about 550 g). The upper layer was separated, and the lower layer was extracted three times with ether (about 1000 ml altogether. The combined extracts were dried with calcined potassium carbonate and filtered. Ether was distilled off through a column, and the residue was fractionated from a flask having a good Vigreux column.

Two fractionations gave 600-630 g (55-59% on the amount of methylhexadienyne taken) of 2,4-dimethyl-2-cyclopenten-1-one, b.p. 50-52° at 9 mm, n_D^{20} 1.4670. The head and tail fractions amounted to 60 g; there was 215-220 g of undistilled residue.

SUMMARY

1. A general method has been developed for the preparation of α,β-unsaturated cyclic ketones. There are two stages: bromination of a cyclic ketone in presence of calcium or magnesium carbonate; and elimination of hydrogen bromide from the bromo ketone formed, which is effected by heating it in presence of diethylaniline.

2. 2-Methyl-2-cyclohexen-1-one (58% yield), 2-methyl-2-cyclopenten-1-one (50% yield), 2-cyclohexen-1-one (35% yield), and 2-cyclopenten-1-one (25% yield) have been prepared by this method.

3. It has been proved that, in the bromination of 2-methylcyclohexanone and of 2-methylcyclopentanone, bromine attacks the tertiary carbon atom, and not a secondary carbon, as asserted previously by some workers.

4. The method of preparing 2,4-dimethyl-2-cyclopenten-1-one has been simplified and improved.

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# SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XVIII. CONDENSATION OF
3,4,4a,7,8,8a-HEXAHYDRO-4a-METHYL-5-VINYL-2(1H)-NAPHTHALENONE AND
3,4,4a,5,6,8a-HEXAHYDRO-8a-METHYL-8-VINYL-2(1H)-NAPHTHALENONE WITH
## 2,4-DIMETHYL-2-CYCLOPENTEN-1-ONE*

I. N. Nazarov and I. V. Torgov

The simple method that we have developed in our laboratory for the preparation of polycyclic compounds having angular methyl groups[1] has made it possible, for the first time, to carry out the total synthesis of steroid ketones belonging to the cis-cis series. An important intermediate product for the synthesis of these compounds is the vinyl-2(1H)-naphthalenone(I),which has been described in detail in a previous communication [2]. By condensation of this substance with 2,4-dimethyl-2-cyclopenten-1-one (III), we have already prepared an isomer of methylandrostenedione [1] although the structure of this has not been established.

In the present work we have made a detailed study of the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2,4-dimethyl-2-cyclopenten-1-one (III). In this condensation, depending on the orientation of the reacting compounds, two series of isomers may be formed: one in which the keto group is in the 17-position (the "normal" structure), and one in which it is in the 15-position (the "inverted" structure):
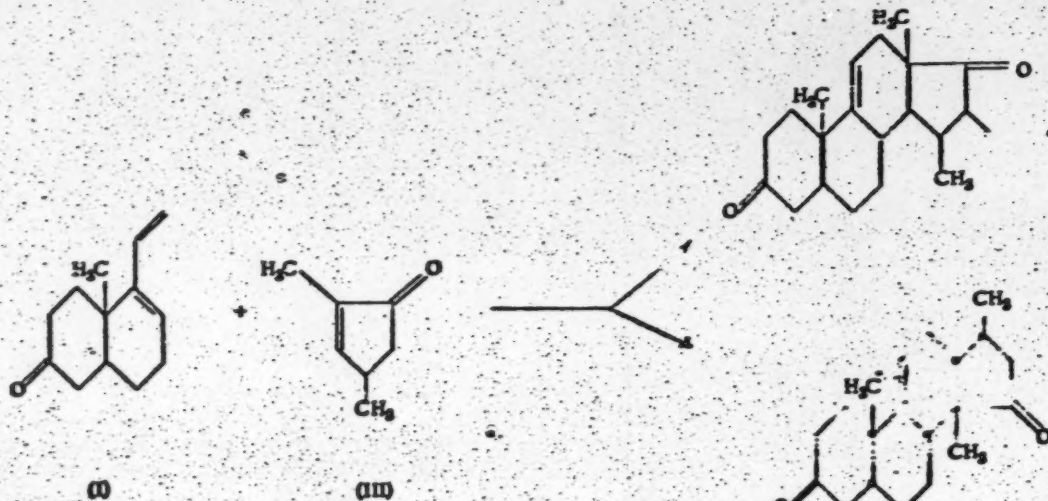
The number of isomers in each series is determined by the number of asymmetric carbon atoms (marked by large dots) and by the cis-addition rule that applies in the diene condensation. It will be readily seen that there is a possibility of obtaining eight racemates in each structural series. For "inverted" structures of the cis-cis series, for example, all of the eight possible racemates are represented below:
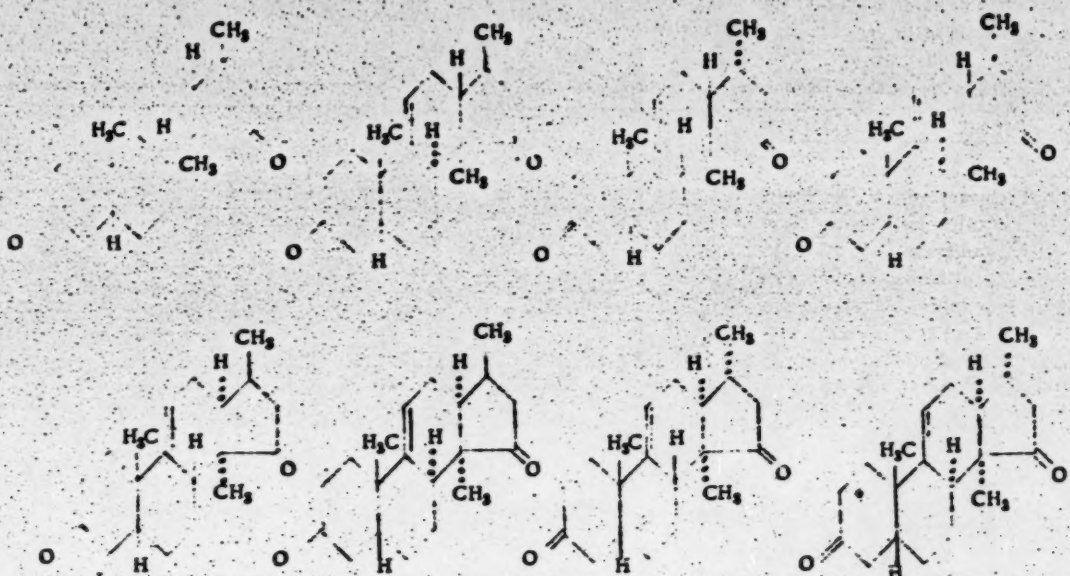

Actually, when the diene (I) was heated with 5-8 times its weight of the dimethylcyclopentenone (III) (170°, 10-13 hours), a 55% yield was obtained of a mixture of isomeric steroid ketones, from which three isomers of 2,14,17-trimethyl-9-cardosterene-3,15-dione (IV A, IV B, and IV C in the proportions of 95:4:1 approximately) were isolated (the nomenclature used here for such synthetic steroids is that proposed by Nazarov [3]). It was found that all three compounds were of "inverted" structure, and the difference between the isomers IV A and IV B was determined by the spatial arrangement of the substituents at $C_{13}-C_{14}$, and that between IV C and IV A lay in the difference in spatial disposition of the hydrogen atom at C_8.

(I)   +   (III)

(IV A)   (IV B)   (IV C)

m.p. 166-167°   m.p. 155-156°   m.p. 203-205°
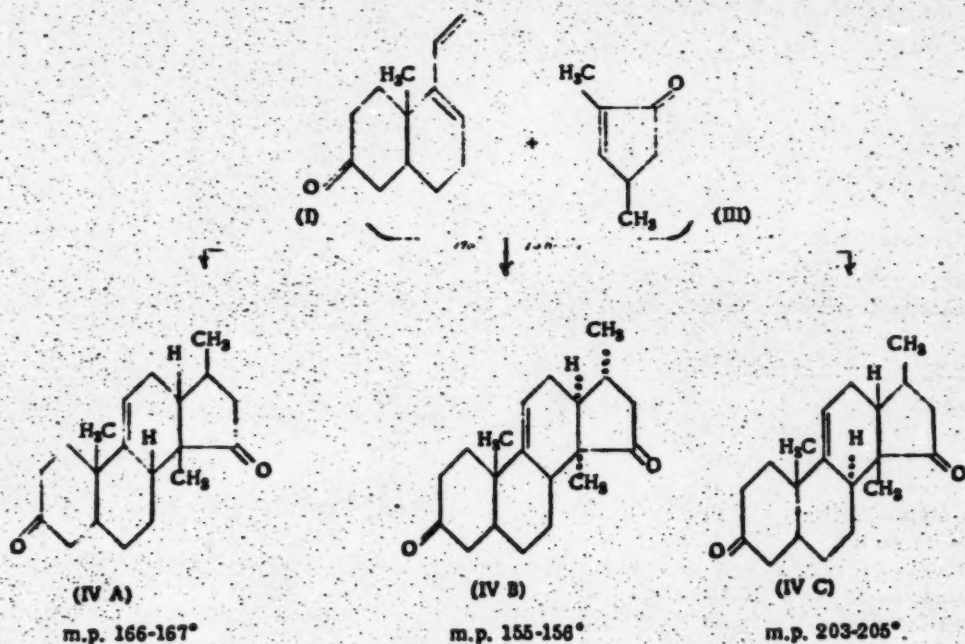
The choice of a spatial configuration for the diketone IV A from among the eight structures given above was made on the basis of the rules of the diene synthesis; for there are no direct proofs of the relative spatial dispositions of the substituents in this diketone. Stuart models that we made of the molecules showed that all eight structures were quite possible.

In the proof of the structures of the steroid diketones obtained, an important part was played by the difference in activity of the keto groups in rings A and D. Whereas the keto group in ring A readily underwent Clemmensen reduction, the keto group in ring D was not affected by this treatment. The inertness of a keto group in the five-membered ring D has been noted on several occasions in the literature. Isomers of estrone and epiandrosterone, for example, which have carbonyl groups in the 16-position, are not reduced under these conditions [4] and reduction of tetrahydro-7a-methyl-1,4(5H)-indandione results in removal of only the keto group in the six-membered ring [5]:
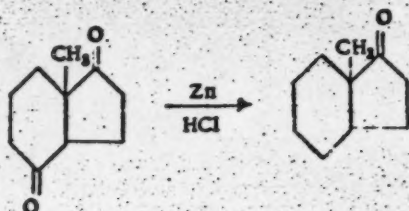

The structure of the diketone IV A was proved by the following series of transformations:
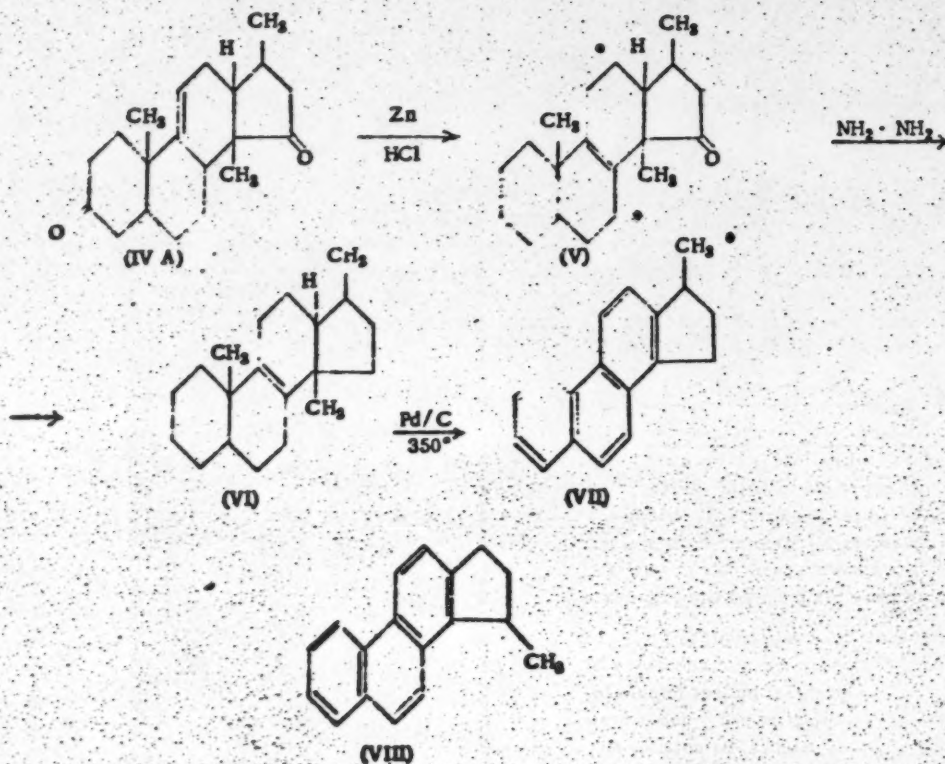
The diketone IV A was converted by Clemmensen reduction into 10,14,17-trimethyl-8-cardosterene-15-one (V), m.p. 104°, which was further converted by the Kizhner reaction into 10,14,17-trimethyl-8-cardosterene (VI). Dehydrogenation of this hydrocarbon in the presence of palladized charcoal followed by chromatographic treatment led to the isolation of the so-called Diels hydrocarbon, 16,17-dihydro-17-methyl-15H-cyclopenta[a]phenanthrene (VII). The melting points of the hydrocarbon and of its compound with trinitrobenzene agreed with the values given in the literature and were greatly different from the corresponding values for 16,17-dihydro-15-methyl-15H-cyclopenta[a]phenanthrene (VIII), which should have been formed if the original diketone had the "normal" structure.

Substance	Melting point (°C)	
	of hydrocarbon	of trinitrobenzene derivative
16,17-Dihydro-15-methyl-15H-cyclopenta[a]phenanthrene	76 – 77[5]	143 – 144[6]
16,17-Dihydro-17-methyl-15H-cyclopenta[a]phenanthrene (Diels hydrocarbon)	125 –126[7]	147[7]
	123 –124[8]	148[6]
	124 –125[9]	150[8]
Hydrocarbon obtained	121.5–122	148

The structure of the diketone IV A was proved also in a second, independent way: namely, by its conversion into phenanthrene derivatives as indicated below:
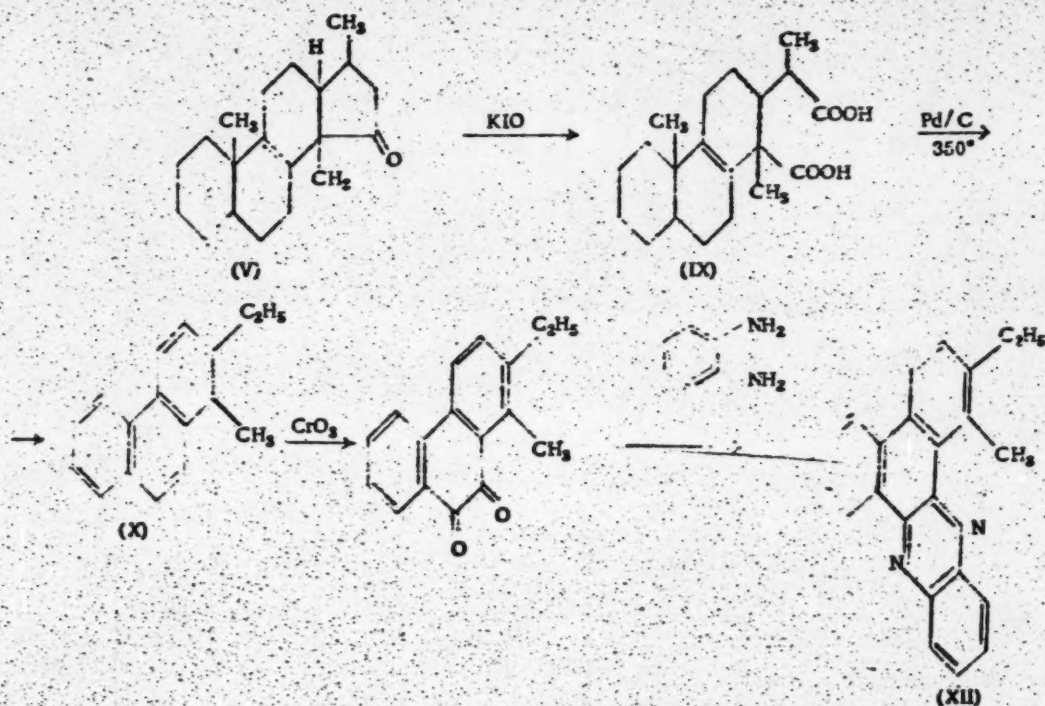
The monoketone (V) was oxidized with alkaline iodine in methanol solution to the dicarboxylic acid (IX) which on dehydrogenation yielded the known 2-ethyl-1-methylphenanthrene (X). (X) was converted into the quinone (XI), and then into the quinoxaline (XII). The melting points of (X) and (XII) agreed with those given in the literature, and they were quite different from those of 1-ethyl-2-methylphenanthrene and its derivative, which would

correspond to the "normal" structure. The melting points of the isomeric quinones are close together and therefore not very characteristic.

Substance	Melting point (°C)		
	of hydrocarbon	of quinone	of quinoxaline
1-Ethyl-2-methylphenanthrene	79–80 [10,11]	157–159	146–147
2-Ethyl-1-methylphenanthrene	100 [10]	163	108
Our 2-ethyl-1-methylphenanthrene	96	155–157	108

The structure of the diketone IV B was proved by the same method. Clemmensen reduction of IV B yielded the monoketone (XIII), m.p. 122°, which was distinct from the monoketone (V). By the series of transformations already described, it was converted into 2-ethyl-1-methylphenanthrene (X), which was characterized by its melting point and by its conversion into the quinone (XI) and the quinoxaline (XII):

(IV B) → Zn HCl → (XIII) → (X)
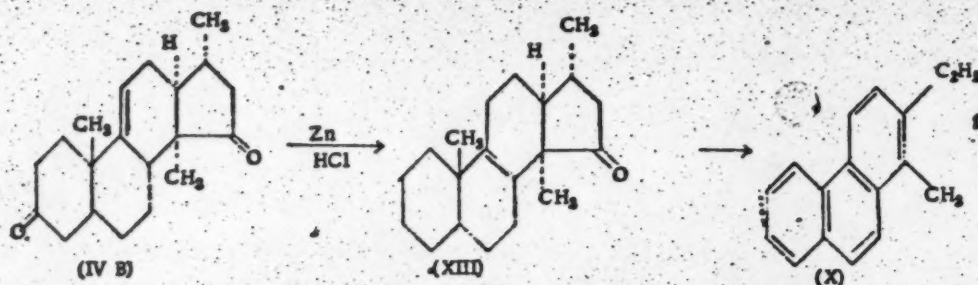
As the monoketones (V) and (XIII) both give the same ethylmethylphenanthrene (X) as a result of analogous transformations, it is evident that they have identical carbon skeletons; the difference between them, and therefore between the original diketones IV A and IV B, must lie only in the spatial dispositions of the hydrogen and methyl at $C_{13} - C_{14}$. We do not consider that the difference between the diketones IV A and IV B can be explained by a difference in the spatial arrangement of the methyl in the 17-position because we shall show in later communications that the condensation of (I) with 2-methyl-2-cyclohexen-1-one and with 2-methyl-2-cyclopenten-1-one leads to the formation of analogous stereoisomers, and yet there is now no methyl group in the 17-position.

The monoketone (XIII) was found to be identical with that obtained by hydrogenation of the condensation product of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (XIV) with 2,4-dimethyl-2-cyclopenten-1-one (III)*:

(XIV) + (III) → (XV) → H₂, Pt C₂H₅OH → (XIII)

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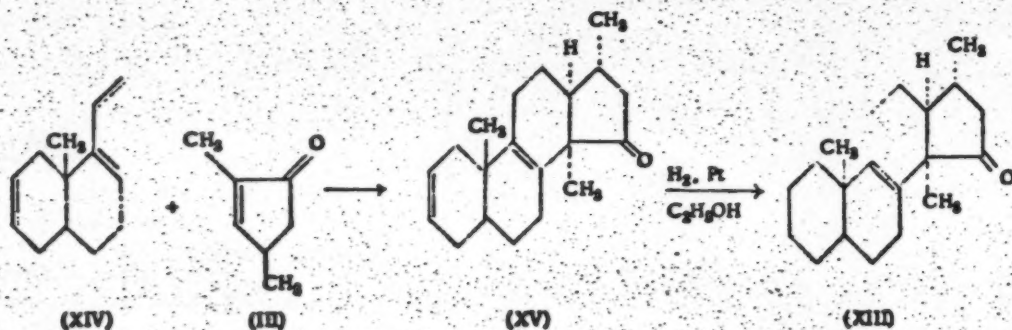
*This condensation is described in the next paper in this journal.

Clemmensen reduction of the isomer IV C gave the same monoketone (V) as that obtained by reduction of the diketone IV A. It is most probable that the difference between the diketones IV A and IV C lies in the spatial disposition of the hydrogen at C_8. Under the conditions of Clemmensen reduction, the double bond is displaced from 8(11) to 8(9) in both isomers, and the same monoketone (V) is therefore obtained.

Displacement of a double bond in the presence of acids and catalysts occurs very readily in polycyclic systems.

Thus the following transformations have been effected in the cholestane series [12]:
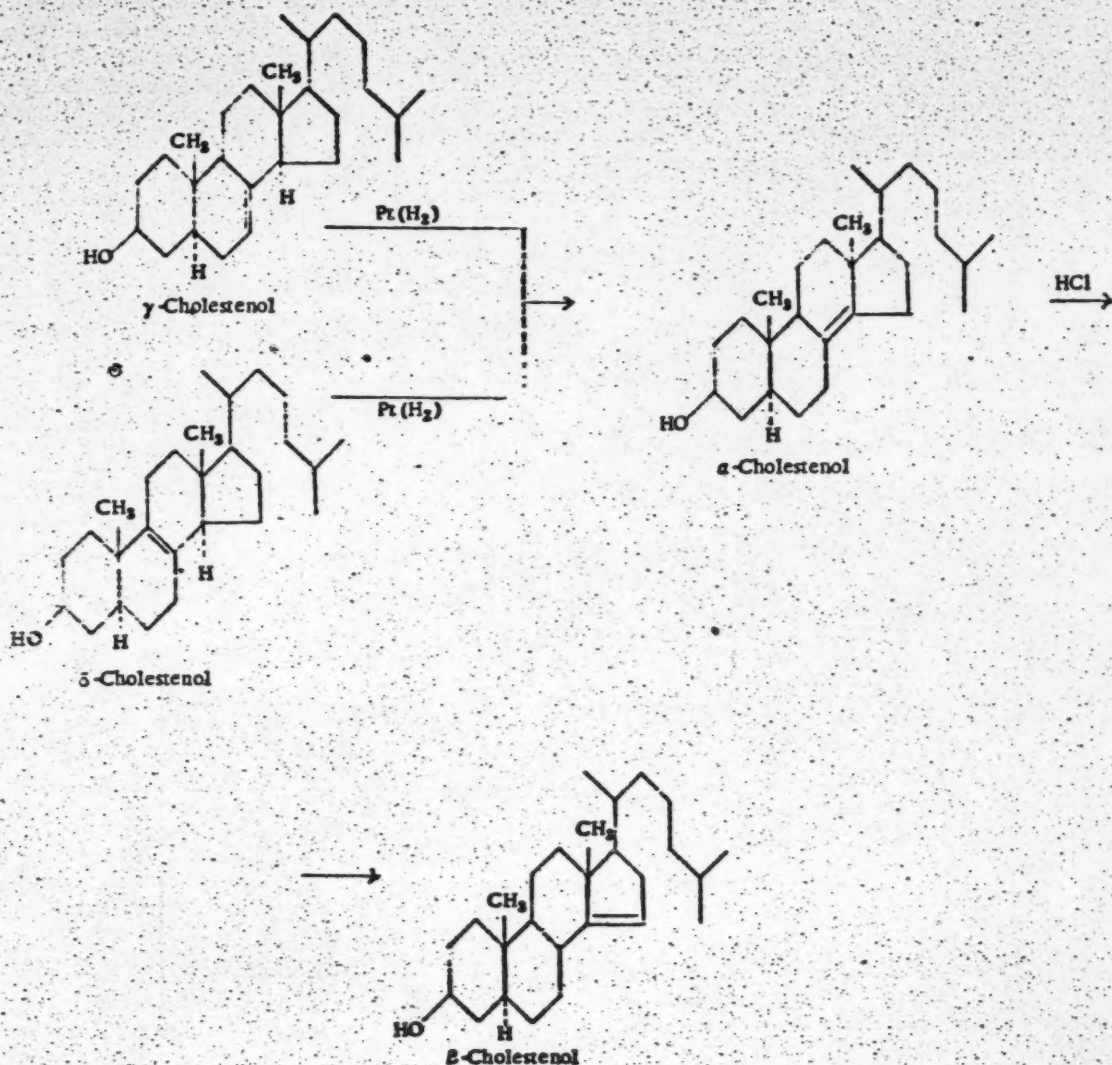
Similar transformations have been effected also for related compounds: ergostenols [13], spinasterols [14], and zymosterol [15]. The case of zymosterol is of particular interest because the analogy with our diketones is here the closest (with respect to the position of the double bond):
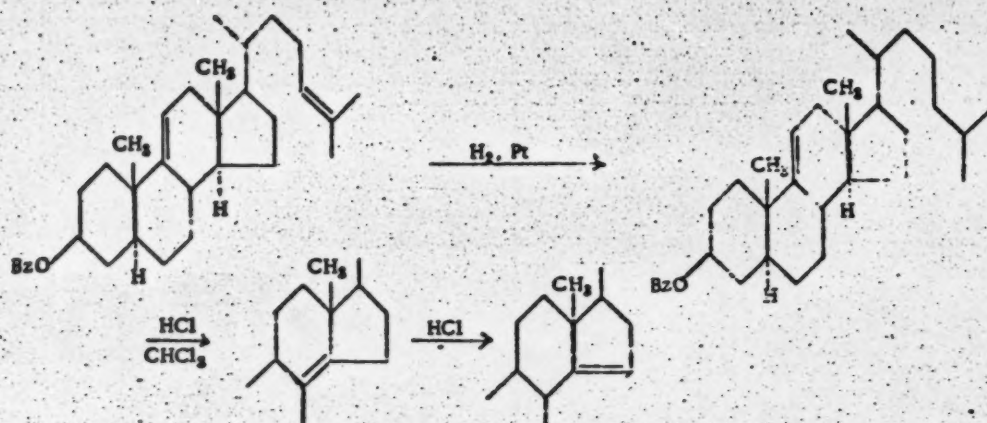
Under the action of hydrogen chloride, equilin is converted, with displacement of a double bond, into 8(9)-dehydroisoestrone, which will undergo reversible isomerization into 9-dehydroestrone [16].
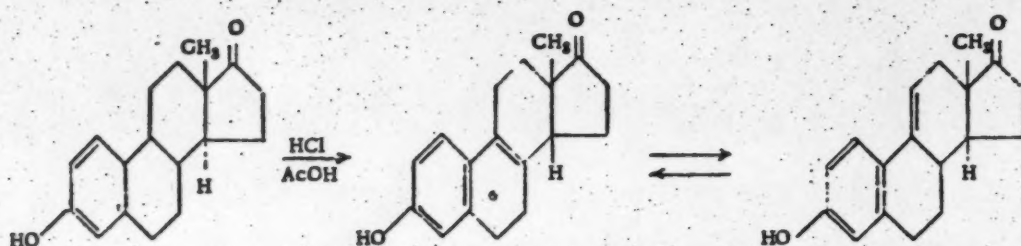
When citraconic anhydride is condensed with 1,2-dihydro-7-methoxy-4-vinylnaphthalene, acids are formed in in which, as Miescher has shown, the double bond is readily displaced to the inter-ring position in presence of hydrogen chloride [17]:
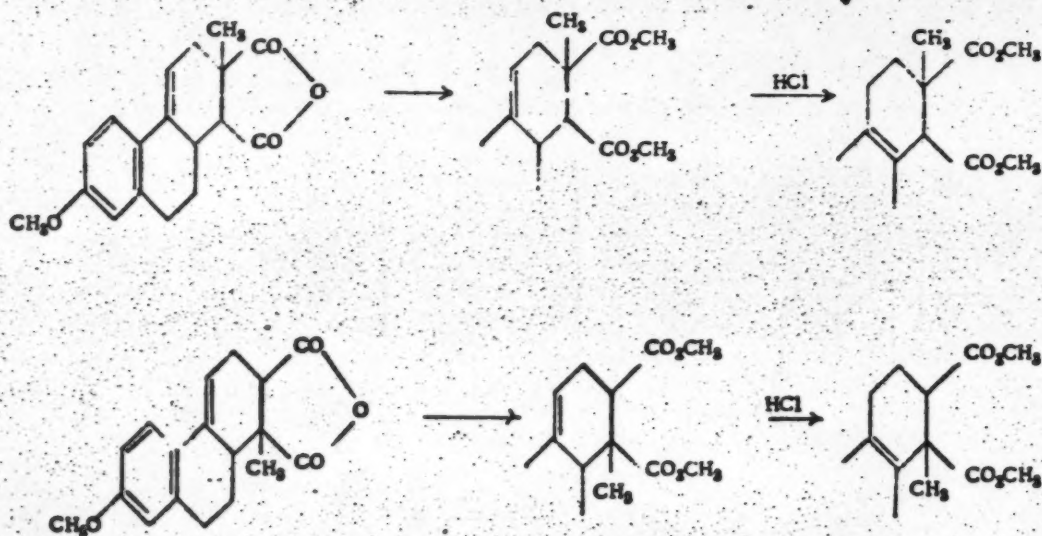
The positions of the double bonds in these compounds were established from absorption spectra. Compounds having an interesting double bond are not hydrogenated in acetic acid in presence of palladized charcoal, whereas the enolid compounds are readily hydrogenated.

When the diketones IV A and IV B were treated with hydrogen chloride in the cold, they were recovered unchanged. However, they readily underwent isomerization with displacement of the double bond when they were heated with a mixture of hydrochloric and acetic acids. Under this treatment the diketones IV A and IV C gave the same isomeric ketone (IV D), whereas the diketone IV B gave two isomeric diketones (IV E and IV F).

It should be noted that none of the isomeric ketones IV A, IV B, IV C, IV D, and IV E could be hydrogenated in alcohol in presence of an Adams platinum catalyst; nor was any shift in the double bond to be noted. When hydrogenated in acetic acid in the presence of the same catalyst, the diketone IV A remained unchanged, and the diketones IV B, IV C, and IV D gave mixtures of noncrystallizing products, which could not be separated chromatographically.

The diketone IV A, on being hydrogenated in acetic acid in the presence of H_2PtCl_6 and palladium carried on barium sulfate, gave a mixture of products, from which it was found possi le to isolate the crystalline hydroxy ketone, 10,14,17-trimethyl-8-cardosteren-3-ol-15-one (XVI). This, on oxidation with chromic anhydride, yielded

(V) m.p. 104°   (IV A) m.p. 166-167°   (XIII) m.p. 122°

(IV D) m.p. 113-114°   (IV B) m.p. 155-156°   (IV E) m.p. 160-161°

(IV F) m.p. 112-113°

(IV C) m.p. 203-205°

Zn, HCl
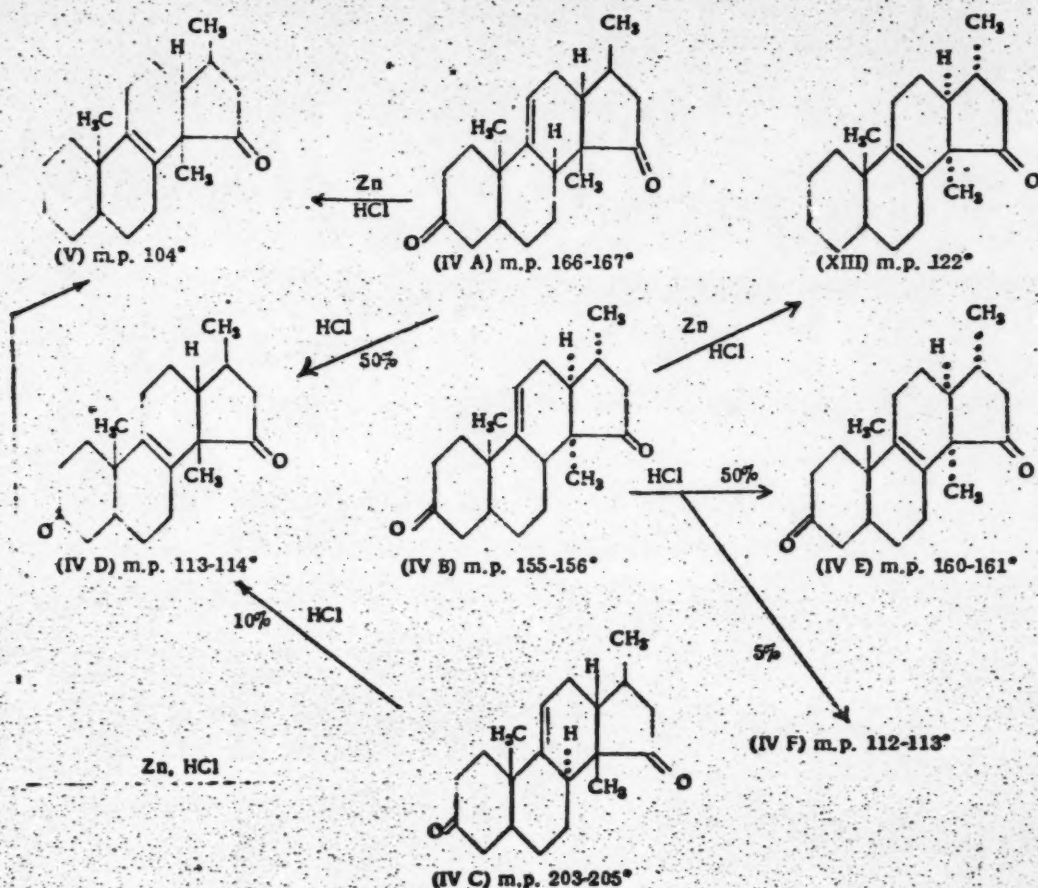
10,14,17-trimethyl-8-cardosteren-3,15-dione (IV D). Under comparatively severe conditions of hydrogenation, therefore, the double bond of the diketone IV A was preserved, being merely displaced from the 9(11)- to the 8(9)-position:

(IV A)
m.p. 166-167°

H₂ Pd/BaSO₄
H₂PtCl₆

(XVI)
m.p. 131-132°

CrO₃
CH₃COOH

(IV D)
m.p. 113°
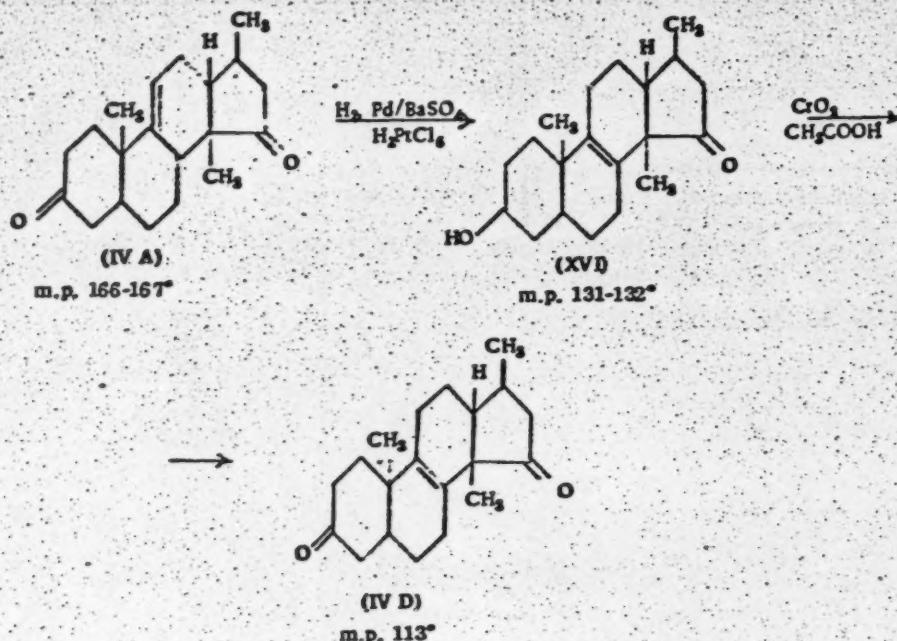
The determination of the positions of double bonds in tetracyclic systems by a chemical method is extremely difficult. For the cholestenols (and the ergostenols similarly) such a determination has been made in two cases only: 7-cholesten-3-ol (γ-cholestenol) [18] and 14-cholesten-3-ol (ß-cholestenol) [19]. In other cases the position of the double bond has been established by comparison of values of specific rotatory power [20].
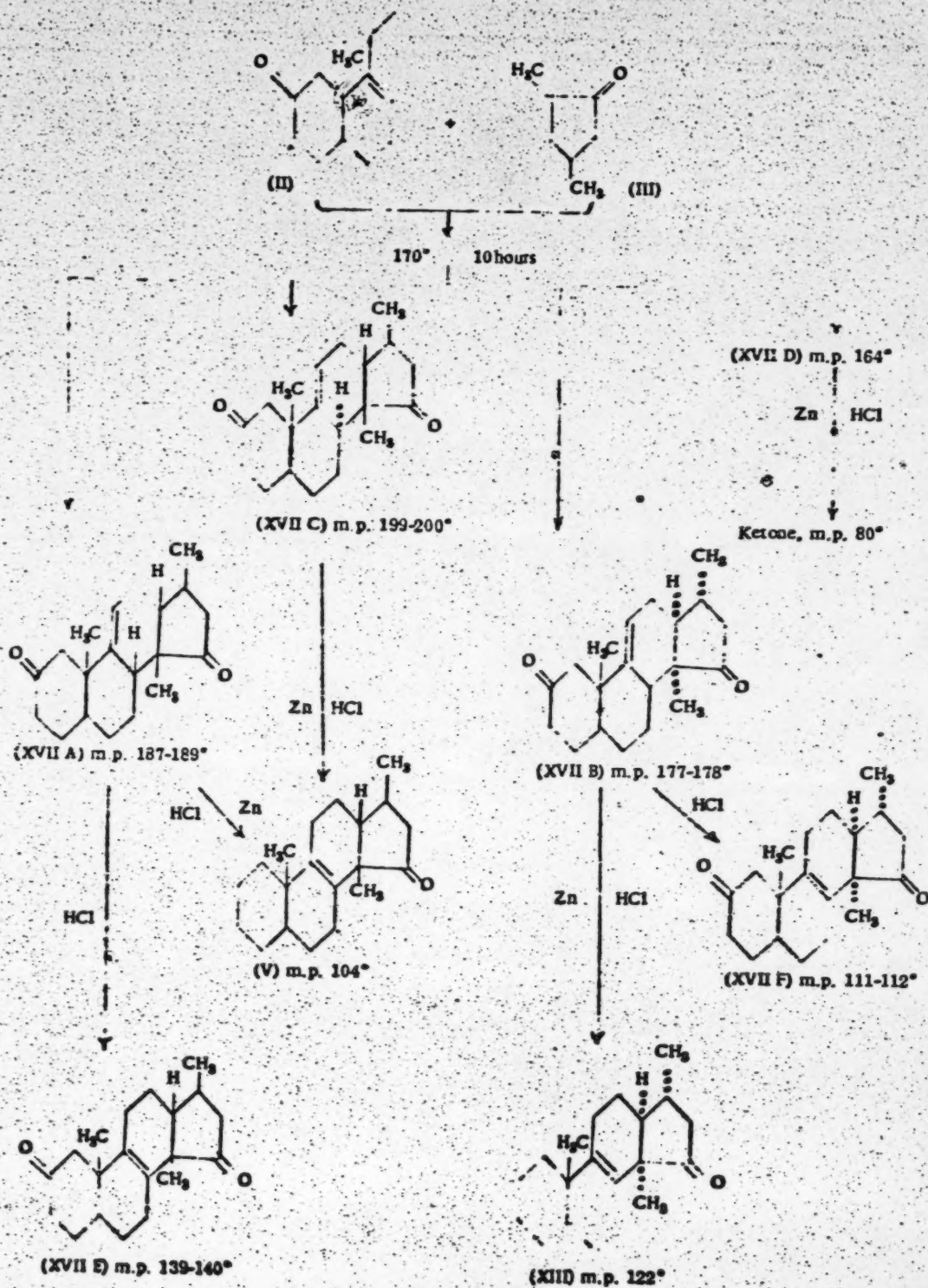
In allotting the positions of the double bonds in the steroid diketones that we have prepared (IV A − E), we have taken the following considerations as our basis: 1. The main reaction product formed over a wide range of temperatures, 130-200°, must have a double bond in the 9(11)-position, since it is not likely that displacement of the double bond will occur at the relatively low temperature of the diene condensation (130°). 2. Under the action of hydrogen chloride the double bond tends to take up a place between the rings (owing to the presence of the angular methyl group, displacement in ring D is excluded). 3. The displacement of the double bond may be a reversible process, even though not readily reversible. On these grounds we consider the formulas given above for the diketones IV A − E to be the most probable ones.

When 3,4,4a,5,6,8a-hexahydro-8a-methyl-7-vinyl-2(1H)-naphthalenone (II) was condensed with 2,4-dimethyl-2-cyclopenten-1-one (III) under similar conditions, a mixture of four isomers (XVII A, XVII B, XVII C, and XVII D) of 10,14,17-trimethyl-9-cardosterene-2,15-dione in the proportions of 60 : 35 : 3 : 2 approximately was formed. The first three steroid diketones have the "inverted" structure, and the structure of the fourth has not been established.

Clemmensen reduction of the diketones (XVII A and XVII C) gave the already known monoketone (V), and their structure is therefore proved. When the isomer (XVII A) was heated with hydrochloric and acetic acids, it was converted partially into the isomer (XVII E). The considerations already applied to the determination of the structures of the diketones IV A and IV C lead us to regard the formulas given above as the most probable ones.

Clemmensen reduction of the diketone (XVII B) yielded the monoketone (XIII) described above so that the spatial configuration of the diketone (XVII B) was identical with that of the diketone (IV B). When the diketone (XVII B) was heated with hydrochloric and acetic acids, isomerization occurred only to a very slight extent, which is in contrast with the behavior of the diketone (IV B), which underwent 50% isomerization. Nevertheless, it was

found possible to obtain a 5% yield of the isomeric diketone (XVII F).

(II)

(III)

170° 10 hours

(XVII C) m.p. 199-200°

(XVII D) m.p. 164°

Zn | HCl

Ketone, m.p. 80°

(XVII A) m.p. 187-189°

Zn | HCl

(V) m.p. 104°

(XVII B) m.p. 177-178°

HCl | Zn

(XVII F) m.p. 111-112°

HCl

Zn | HCl

(XVII E) m.p. 139-140°

(XIII) m.p. 122°

Clemmensen reduction of the isomer (XVII D) yielded a monoketone of m.p. 80°, which was different from the monoketones (V) and (XII). The amount of the original diketone available was too small to permit further investigation; the most that can be said is that it has a different structure from that of the other isomers. The diketones (XVII A), (XVII B), and (XVII C) do not undergo hydrogenation in the presence of an Adams platinum catalyst, neither in alcohol nor in acetic acid.

Hence, when the dienes (I) and (II) are condensed with the dimethylcyclopentanone (III), there are formed in every case a mixture of isomeric steroid ketones of inverted structure, which differ among themselves only in the spatial disposition of substituents at $C_{13}-C_{14}$ or the spatial disposition of hydrogen at C_8.

EXPERIMENTAL

3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) (b.p. 100-103° at 1 mm; n_D^{20} 1.5260) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) (b.p. 106-107° at 1.5 mm, n_D^{20} 1.5270) were prepared by the method described in a previous communication [2]. 2,4-Dimethyl-2-cyclopenten-1-one (III) was prepared by the cyclization of 2-methyl-1,5-hexadien-3-one, as described previously [21] (b.p. 58-59° at 15 mm; n_D^{20} 1.4675). The melting points of all substances described in this paper were determined in a copper block; all temperatures are corrected.

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2,4-Dimethyl-2-cyclopenten-1-one (III)

A mixture of 12.3 g of the dienone (I) and 96 g of the dimethylcyclopentenone (III) was heated in an atmosphere of carbon dioxide in sealed tubes for 13 hours at 170°. The excess (83 g) of the dimethylcyclopentenone was distilled off in a water bath at a residual pressure of 15 mm, and the residue was mixed with 20 ml of petroleum ether and 1 ml of benzene. Crystallization set in immediately. After one day the crystals that had separated were filtered off under suction and washed with a mixture of petroleum ether and benzene (10:1). In this way 7.9 g of a mixture of isomers of m.p. 130-140° was obtained. The mother liquor was evaporated down under reduced pressure, and residual dimethylcyclopentenone (2.0 g) was removed in a water bath at 1 mm residual pressure. The residue was diluted with 5 ml of petroleum ether and then set aside at 8-10° for two days. A second crop of crystals separated (0.15 g; m.p. 156-200°). The second mother liquor was evaporated down, and excess of dienone (2.7 g; n_D^{20} 1.5235) was distilled off at 1 mm and at a bath temperature of not above 150°; the residue was dissolved in a mixture of 3 ml of petroleum ether and 1 ml of benzene. After two days a third crop of crystals was separated (0.3 g; m.p. 140-150°). In this way 8.35 g altogether of a mixture of crystalline isomers of 10,14,17-trimethyl-9-cardosterene-3,15-dione was obtained. The yield was 49% on the amount of the dienone (I) taken, or 55% on the amount of dienone that reacted.

By fractional crystallization of the first and third batches of crystals from a mixture of petroleum ether and benzene (3:1), 6.7 g of isomer (IV A), m.p. 166-167°, and 0.15 g of isomer (IV B), m.p. 156-156.5°, were isolated. Their separation was rendered difficult by the fact that they have almost the same solubility and separate out together. By a combination of slow crystallization with mechanical separation of the required isomers, it was found possible to effect the separation. In other experiments somewhat greater amounts of the isomer (IV B) [with respect to the isomer (IV A) were obtained than those shown above. In one experiment, for example, 0.12 g of isomer (IV B) was obtained together with 1.6 g of isomer (IV A). The isomer (IV A) has been isolated and characterized previously [1]. The isomer (IV B) forms white plates, m.p. 156-156.5°.

Found %: C 79.8; 79.8; H 9.45; 9.6
$C_{20}H_{28}O_2$. Calculated %: C 80.0   H 9.4

A mixture of isomers (IV A) and (IV B) melts at 130-140°.

By crystallization of the second crop of crystals from a mixture of methanol and benzene (3:1), 70 mg of the isomer (IV C), m.p. 203-205°, was isolated in the form of white needles.

Found %: C 80.1; 80.25; H 9.4; 9.5
$C_{20}H_{28}O_2$. Calculated %: C 80.0;   H 9.4

Isomerization of the Diketone (IV A)

A mixture of 260 mg of the diketone (IV A), m.p. 166-167°, 5 ml of acetic acid, 5 ml of concentrated hydrochloric acid, and 6 ml of toluene was boiled under reflux for ten hours. The toluene layer was separated, and the

aqueous layer was diluted with an equal amount of water and extracted with benzene. The combined benzene-toluene extracts were neutralized by agitation with 10% caustic soda. After removal of solvent under reduced pressure, the residue was crystallized from 1 ml of alcohol, yielding 140 mg of the diketone (IV D) in the form of large prisms, m.p. 114-115°.

<div align="center">

Found %: C 79.8; 80.2; H 9.6; 9.6

$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

</div>

When a solution of the diketone (IV A) in acetic acid was treated with hydrogen chloride in the cold for 12 hours, no isomerization occurred, and the substance was recovered unchanged. In a similar way, no isomerization occurred when a xylene solution of the diketone (IV A) was heated at 170° for seven hours.

Isomerization of the Diketone (IV B)

This reaction was carried out similarly to the preceding one. From 285 mg of the diketone (IV B), m.p. 156-156.5°, 130 mg of the diketone (IV E) was obtained in the form of long prisms (from alcohol), m.p. 161-162°.

<div align="center">

Found %: C 79.9; 79.8; H 9.4; 9.3

$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

</div>

The diketone (IV E), when mixed with the original diketone (IV B) or with the diketone (IV A), gave a strongly depressed melting point. From the mother liquor 15 mg of the isomer (IV F) was isolated in the form of needles, m.p. 112-113° (from alcohol).

<div align="center">

Found %: C 80.1; 79.8; H 9.5; 9.4

$C_{20}H_{28}O_2$. Calculated %: C 80.0; H 9.4

</div>

A mixture melting point test of (IV F) and (IV D) gave a strong depression. An attempt to isomerize the diketone (IV B) by the action of hydrogen chloride in acetic acid at 20° was not successful; the diketone was returned unchanged.

Isomerization of the Diketone (IV C)

The isomerization was carried out in a similar way on 70 mg of the substance of m.p. 203-205°. The diketone was found to be fairly stable, and part of it (30 mg) was recovered after the experiment in an impure form (m.p. 190-200°). It was found possible to isolate 6 mg of the diketone (IV D), m.p. 115-116°, from the mother liquor. In admixture with the diketone (IV D) obtained above, there was no depression in melting point.

Clemmensen Reduction of the Diketone (IV A)

A mixture of 2 g of the diketone (IV A), m.p. 166-167°, 25 ml of acetic acid, 25 ml of concentrated hydrochloric acid, 20 ml of toluene, and 10 g of amalgamated zinc was boiled for 3 hours, 30 minutes under reflux. More zinc was then added (3.5 g), and the mixture was boiled for a further three hours. The reaction mixture was cooled, the toluene layer was separated, and the water layer was extracted three times with ether. The ether and toluene layers were united, neutralized by agitation with a 5% solution of caustic soda, and filtered. The solvent was driven off, and the residue was diluted with 7-8 ml of ether and set aside in the cold to crystallize, when 1.0 g (52%) of the ketone (V) was obtained in the form of white plates, m.p. 100-102°. The pure ketone melted at 103-104° (from petroleum ether).

<div align="center">

Found %: C 83.9; 83.75; H 10.8; 10.6

$C_{20}H_{34}O$. Calculated %: C 83.85; H 10.6

</div>

The dinitrophenylhydrazone formed beautiful yellow needles, m.p. 232-233° (from alcohol).

Clemmensen Reduction of the Diketone (IV C)

A mixture of 75 mg of the diketone (IV C), m.p. 203-205°, 5 ml of acetic acid, 10 ml of concentrated hydrochloric acid, 5 ml of toluene, and 1.5 g of amalgamated zinc was boiled for 3 hours, 30 minutes under reflux.

The toluene layer was separated, and the aqueous layer was extracted twice with benzene. The combined extracts were neutralized, and solvent was driven off under reduced pressure. The residue rapidly crystallized out. Crystallization from 0.5 ml of ether at −15° yielded 21 mg of the ketone (V), m.p. 100-101°. A mixture melting point with a sample of the ketone obtained in the preceding experiment was not depressed.

Clemmensen Reduction of the Diketone (IV B)

The reduction was performed as in the preceding experiments. From 400 mg of the diketone (IV B), m.p. 156-156.5°, 50 mg of the ketone (XIII), m.p. 120-122° (from hexane), was obtained.

Found %: C 83.9; H 10.8
$C_{20}H_{34}O$. Calculated %: C 83.85; H 10.6

A mixture melting point with the ketone obtained by hydrogenation of the ketone (XV) and having m.p. 122° was not dpressed. The mother liquor remaining after the separation of the ketone (XIII) crystallized out almost complete. It was used without purification for the oxidation reaction.

Kizhner Reduction of the Ketone (V)

To a solution of 1.7 g of the ketone (V), m.p. 100-102°, in 5 ml of dioxane, 1.2 ml of hydrazine hydrate and 5 ml of diethylene glycol were added, and the mixture was heated for a few minutes in a water bath. It was then transferred to a Favorsky flask having ground joints, a solution of 1.4 g of sodium in 36 ml of diethylene glycol was added, and the almost homogeneous mixture was heated at 205-210° in a feeble current of nitrogen for 15 hours. Several milliliters of distillate came over. The reaction mixture was diluted with 50 ml of water and extracted twice with 50 ml portions of ether. The ether extract was shaken with 10% hydrochloric acid and dried with magnesium sulfate. The ether was driven off, and the residue was vacuum distilled, yielding 1.3 g (81%) of the hydrocarbon (VI) as a colorless liquid, not very viscous and almost odorless, b.p. 130-135° at 1 mm, n_D^{20} 1.5200.

Found %: C 87.9; 88.15; H 11.9; 12.1
$C_{20}H_{32}$ Calculated %: C 88.2; H 11.8.

Dehydrogenation of the Hydrocarbon (VI)

A mixture of 1.1 g of the hydrocarbon (VI), 0.5 g of palladized charcoal (10% Pd), and 18 ml of dry benzene was heated in a nitrogen atmosphere in a rotating autoclave at 350° for six hours, the initial pressure being 30 atm. The reaction mixture was filtered, benzene was removed under reduced pressure, and the noncrystallizing residue was dissolved in 10 ml of petroleum ether and submitted to chromatography on 10 g of aluminum oxide, when the following fractions were obtained:

Fractions I — III	Each 4 ml of petroleum ether	587 mg	Oil
Fractions IV — VI	Ditto	129 mg	Crystals impregnated in oil, m.p. 80-85°
Fractions VII—VIII	Ditto	42 mg	Crystals, m.p. about 100°
Fractions IX — XI	Each 4 ml of a mixture of petroleum ether and benzene (7:1)	97 mg	Crystals impregnated in oil
Fractions XII — XIII	Each 4 ml of a mixture of petroleum ether and benzene (3:1)	9 mg	Oil
Fraction XIV	Each 4 ml of a mixture of petroleum ether and benzene (1:1)	2 mg	Ditto
Fractions XV — XVI	Each 4 ml of a mixture of petroleum ether and benzene (1:3)	9 mg	Ditto
Fractions XVII — XVIII	Each 4 ml of benzene	6 mg	Ditto
	Total	881 mg	

Crystallization of fractions VII — XI from 1 ml of petroleum ether yielded 25 mg of nodular crystals, m.p. 111-113.5°. A second crystallization from 0.5 ml of petroleum ether yielded 10 mg of the Diels hydrocarbon (VII), m.p. 121.5-122°.

Found %: C 92.85; 92.8; H 7.0; 7.1
$C_{18}H_{16}$ Calculated %: C 93.06; H 6.94

With trinitrobenzene it formed yellow needles, m.p. 148-149° (from methanol).

The mother liquors from the crystallizations were combined with Fractions IV —VI, and the mixture was crystallized from 0.7 ml of petroleum ether. A further 41 mg of the Diels hydrocarbon (VII), m.p. 118-119°, was obtained. Recrystallization of this from petroleum ether yielded 20 mg of pure hydrocarbon (VII), m.p. 120.5-121°.

Oxidation of the Ketone (V) to the Dicarboxylic Acid (IX)

To a stirred solution of 0.8 g of the ketone (V) in 10 ml of methanol, solutions of 2.1 g of iodine in 25 ml of methanol and of 4 g of caustic potash in 8 ml of water and 15 ml of methanol were added simultaneously in such a way that iodine was always present in excess. The addition was complete in 20 minutes, and the mixture was then set aside for two hours. The greater part of the methanol was distilled off under reduced pressure, and 10 ml of water was added. The solution was acidified to Congo red, and the precipitated yellow mass was extracted three times with ether. The ether extracts were carefully washed with a 10% thiosulfate solution until decolorized, and were then filtered. The ether was removed, and 5 ml of methanol and 4 ml of 30% caustic soda were added to the residue. The brown solution was heated under reflux for four hours in a water bath. The methanol was removed, and the residue was diluted with water (5 ml), extracted twice with ether to remove neutral products, and acidified with 20% hydrochloric acid (10 ml) cooled to −5°. After one hour the yellow precipitate formed was filtered off under suction and washed with ice water. Crystallization from 5 ml of acetic acid yielded 0.39 g (41%) of the acid (IX) in the form of a white powder, m.p. 199-202°.

$$\text{Found \%:} \quad C\ 71.75;\ 71.5;\quad H\ 9.35;\ 9.25$$
$$C_{20}H_{30}O_4\ \text{Calculated \%:}\ C\ 71.85;\quad H\ 9.05$$

Dehydrogenation of the Acid (IX)

A mixture of 0.33 g of the acid (IX), 8 ml of benzene, and 0.6 g of 10% palladized charcoal was heated in a rotating autoclave in an atmosphere of nitrogen (initial pressure 20 atm) at 350° for 11 hours. The reaction mixture was filtered, the benzene was distilled off, and the residue was dissolved in 1 ml of petroleum ether. The solution, on cooling, gave a crystalline precipitate, which was filtered off under suction and washed with petroleum ether. On account of its high solubility, only 10 mg of 2-ethyl-1-methylphenanthrene (X), m.p. 95-96°, could be isolated.

$$\text{Found \%:} \quad C\ 92.9;\ 92.9;\quad H\ 7.2;\ 7.2$$
$$C_{17}H_{16}\ \text{Calculated \%:}\ C\ 92.7;\quad H\ 7.3$$

The mother liquor, on being cooled to −70°, yielded a further 38 mg of hydrocarbon, m.p. 85-88°.

A solution of 22 mg of 2-ethyl-1-methylphenanthrene (X) of m.p. 85-88° in 1 ml of acetic acid was mixed with a solution of 50 mg of chromic anhydride in 1 ml of acetic acid. The mixture was heated at 100° for ten minutes, and then cooled. Water (1 ml) was added, and the mixture was heated until the turbidity present disappeared. It was then set aside to crystallize, and on the next day 10 mg of 2-ethyl-1-methyl-9,10-phenanthrenequinone (XI) came down. Crystallization from 0.5 ml of methanol yielded 4 mg of pure quinone (XI), m.p. 155-157°. The quinoxaline (XII), which was prepared by heating the quinone (XI) with o-phenylenediamine in methanol in the presence of a drop of acetic acid, is a yellow crystalline substance, m.p. 108-109° (from methanol).

Oxidation of the Ketone (XIII) and Dehydrogenation of the Acid Formed

The ketone (XIII) (1.2 g) was oxidized with iodine in alkaline solution, as described above. A dicarboxylic acid (450 mg) was obtained, and this was dehydrogenated under the conditions described above for 12 hours. yielding 48 mg of 2-ethyl-1-methylphenanthrene (X), m.p. 85-88°. Without further purification, this was oxidized with chromic anhydride in acetic acid, yielding 7 mg of the quinone (XI), m.p. 155-156°. The quinoxaline prepared from this quinone melted at 105-107°; the mixture melting point with the quinoxaline (XII) from the preceding experiment was not depressed.

Hydrogenation of the Diketones (IV A), (IV B), (IV C), and (IV D), in Presence of an Adams Platinum Catalyst

The diketones IV A, IV B, IV C, and IV D did not undergo hydrogenation in alcoholic solution in presence of an Adams platinum catalyst. When the diketone IV A was submitted to the hydrogenation treatment in acetic acid. it was not affected. When the diketones IV B, IV C and IV D were hydrogenated in acetic acid (30-100 mg of diketone, 10-20 mg of PtO$_2$ 3-5 ml of acetic acid; 3 hours), a noncrystallizing mixture was obtained in each case. Attempts to separate these mixtures chromatographically were not successful.

Hydrogenation of the Diketone IV A in Presence of Palladium on Barium Carbonate and Chloroplatinic Acid

A solution of 1.0 g of the diketone IV A of m.p. 166-167° in 10 ml of acetic acid was shaken in an atmosphere of hydrogen in presence of 0.5 g of Pt/BaSO$_4$ for one hour. No hydrogenation occurred; it began only when a few drops of a concentrated H$_2$PtCl$_6$ solution had been added. In the course of ten minutes, 150 ml of hydrogen (24°, 760 mm) was absorbed, and absorption then ceased. The solution was filtered, diluted with

three times its volume of water, and extracted with benzene. The benzene extracts were washed with a 2% solution of caustic soda until neutral, and the benzene was removed under reduced pressure. A small amount of petroleum ether was added to the residual viscous liquid, and it then partially crystallized out, yielding 110 mg of white crystals, m.p. 147-149° According to analysis, this was a mixture (or molecular compound) of the hydroxy ketone XVI and its acetic ester.

<div align="center">

Found %: C 78.0; 77.7; H 9.7; 9.5

$C_{28}H_{18}O_2 \cdot C_{28}H_{28}O(OCOCH_3)$. Calculated %: C 78.0   H 9.6

</div>

These crystals were dissolved in 2 ml of alcohol and 0.2 ml of 10% NaOH was added. The mixture was heated for five minutes in a water bath and then diluted with an equal amount of water. Crystals of the hydroxy ketone XVI quickly made their appearance: they were filtered off under suction, washed with water, and vacuum-dried. The product was 60 mg of the hydroxy ketone XVI, m.p. 131-132°.

<div align="center">

Found %: C 79.3; 79.4; H 10.2; 10.2

$C_{28}H_{28}O_2$ Calculated %: C 79.4;   H 10.0

</div>

Oxidation of the Hydroxy Ketone XVI

A solution of 35 mg of the hydroxy ketone XVI in 0.4 ml of acetic acid was mixed with a solution of 9 mg of chromic anhydride in 0.8 ml of acetic acid, and the mixture was set aside for two days. The solution was diluted with three times its volume of water and extracted with ether. The ether extracts were shaken with caustic soda solution until neutral, and the ether was distilled off. In a short time the residue partially crystallized out, yielding 8 mg of crystals of the diketone IV D, m.p. 111-113°, undepressed by admixture of some of the diketone IV D obtained as described above.

Condensation of 3,4,4a,5,6,8a-Hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2,4-Dimethyl-2-cyclopenten-1-one (III)

A mixture of 12.0 g of the dienone II and 66 g of the dimethylcyclopentenone III was heated in an atmosphere of nitrogen in sealed tubes at 170° for 10 hours 30 minutes. Excess of the ketone III was then removed under reduced pressure in a water bath until crystallization set in (44 g was distilled over). Petroleum ether (10 ml) and benzene (1 ml) were added to the crystallizing residue, and after two hours the precipitated crystals were filtered off under suction and washed with a cold mixture of petroleum ether and benzene (10 : 1). The product was 4.1 g of pure diketone XVII A in the form of white needles, m.p. 187-189° The mother liquor remaining after separation of these crystals was evaporated down, and 13 g of dimethylcyclopentenone was driven off under reduced pressure in a water bath; the residue was poured into a mixture of 10 ml of petroleum ether and 2 ml of benzene. A second crop of crystals was obtained, and after one hour these were filtered off under suction and washed with a mixture of petroleum ether and benzene (10 : 1), yielding 4.6 g of a crystalline powder, m.p. 144-159°. The second mother liquor was evaporated down, diluted with 10 ml of petroleum ether, and set aside for one day. A third crop of crystals (0.4 g) was obtained; m.p. 155-190°. The third mother liquor was evaporated down, and unchanged dienone II was distilled off at a residual pressure of 0.5 mm, the bath temperature being not above 130° (1.6 g of dienone was obtained). The residue was dissolved in a mixture of 5 ml of petroleum ether and 1.5 ml of benzene, and was set aside at 0-3°. Crystals were very slowly precipitated, and after ten days this fourth batch of crystals was filtered off at the pump and washed with petroleum ether (1.0 g; m.p. 130-150°). In this way altogether 10.1 g of a mixture of crystalline isomers of 10,14,17-trimethyl-9(11)-cardostene-2,15-dione was obtained, the yield being 53% on the amount of the dienone II taken for reaction, and 61% on the amount of the dienone II that reacted.

By fractional crystallization from a mixture of petroleum ether and benzene in conjunction with mechanical sorting of the crystals, the second batch of crystals yielded the diketone XVII A, m.p. 187-189°, and the diketone XVII B, m.p. 177-178°. In a similar way, the third batch of crystals gave the isomer XVII C, m.p. 199-200°, and the fourth batch of crystals yielded the isomers XVII B, m.p. 177-178°, and XVII D, m.p. 163-164°. Altogether, the following amounts were isolated in the pure state: 4.86 g of XVII A, 2.57 g of XVII B, 0.25 g of XVII C, and 0.16 g of XVII D.

The isomer XVII A: needles, m.p. 187-189°.

<div align="center">

Found %: C 79.8; 79.6; H 9.8; 9.4

$C_{28}H_{28}O_2$ Calculated %: C 80.0;   H 9.4

</div>

The isomer XVII B: large prisms, m.p. 177-178°.

<div align="center">

Found %: C 80.1; 80.05; H 9.35; 9.4

$C_{28}H_{28}O_2$ Calculated %: C 80.0;   H 9.4

</div>

The isomer XVII C: plates, m.p. 199-200°.

$$\text{Found \%: } C\ 80.2;\ 80.2;\ H\ 9.4,\ 9.4$$
$$C_{28}H_{38}O_2 \qquad \text{Calculated \%: } C\ 80.0; \qquad H\ 9.4$$

The isomer XVII D: cubes, m.p. 163-164°.

$$\text{Found \%: } C\ 80.0;\ 80.2;\ H\ 9.45;\ 9.4$$
$$C_{28}H_{38}O_2 \qquad \text{Calculated \%: } C\ 80.0; \qquad H\ 9.4$$

A mixture of XVII A and XVII B melted at 160-170°, and a mixture of XVII A and XVII C at 160-165°.

Isomerization of the Diketone XVII A

A mixture of 500 mg of the diketone XVII A of m.p. 187-189°, 10 ml of acetic acid, 20 ml of concentrated hydrochloric acid, and 10 ml of toluene was boiled under reflux for four hours. The toluene layer was separated, and the water layer was extracted with benzene. The united benzene-toluene extracts were neutralized by agitation with a 5% solution of caustic soda, the solvent was driven off under reduced pressure, and the dry residue was crystallized from alcohol, yielding 400 mg of unchanged diketone XVII A. By slow crystallization of the mother liquor in conjunction with mechanical selection of the crystals, it was found possible to isolate 70 mg of the isomeric diketone XVII E in the form of fine colorless plates, m.p. 139-141°.

$$\text{Found \%: } C\ 80.0;\ H\ 9.5,\ 9.6$$
$$C_{28}H_{38}O_2 \qquad \text{Calculated \%: } C\ 80.0;\ H\ 9.4$$

Heating of the diketone XVII A in xylene at 170° for ten hours did not cause it to isomerize. Even the last batches of crystals from the mother liquor melted at 188-190°, and showed no depression in admixture with the original diketone XVII A.

Isomerization of the Diketone XVII B

The diketone XVII B of m.p. 177-178° (190 mg) was given the same isomerization treatment, but the boiling lasted ten hours. About 100 mg of the original diketone was recovered unchanged. By slow crystallization of the mother liquor and mechanical selection of crystals, about 20 mg of the isomeric diketone XVII F was isolated as colorless needles, m.p. 111-112°.

$$\text{Found \%: } C\ 80.0,\ H\ 9.5$$
$$C_{28}H_{38}O_2 \qquad \text{Calculated \%: } C\ 80.0;\ H\ 9.4$$

Clemmensen Reduction of the Diketone XVII A

A mixture of 1.0 g of the diketone XVII A, m.p. 187-189°, 25 ml of acetic acid, 37 ml of concentrated hydrochloric acid, 15 ml of toluene, and 10 g of amalgamated zinc filings was boiled under reflux for five hours. The reaction mixture was diluted with 30 ml of water, the toluene layer was separated, and the water layer was extracted twice with benzene. The united extracts were neutralized by agitation with 10% caustic soda, and the solvent was removed under reduced pressure. The residue was dissolved in 3 ml of ether and set aside in the cold to crystallize: the solution yielded 0.12 g (14%) of crystals of the ketone V, m.p. 99-100°. Crystallization from alcohol raised the melting point to 101-102°. In admixture with the ketone V obtained by reduction of the diketone IV A it showed no depression in melting point. Its dinitrophenylhydrazone melted at 229-231° and showed no melting point depression in admixture with the dinitrophenylhydrazone of the ketone V obtained previously.

Clemmensen Reduction of the Diketone XVII C

Reduction of 80 mg of the diketone XVII C of m.p. 199-200°, carried out as above, yielded 10 mg of the ketone V, m.p. 103-104° (no depression with previously prepared ketone V).

Clemmensen Reduction of the Diketone XVII B

The reduction was performed similarly to that of the diketone XVII A. From 0.8 g of the diketone XVII B, m.p. 177-178°, 80 mg of the ketone XIII, m.p. 109-112° was obtained. Crystallization from a mixture of alcohol and petroleum ether gave crystals of m.p. 119-121°. A mixture melting point with the ketone XIII obtained previously from the diketone IV B was not depressed. The dinitrophenylhydrazone formed orange needles, m.p. 215-217°.

Clemmensen Reduction of the Diketone XVII D

Clemmensen reduction of the diketone XVII D of m.p. 163-164° (65 mg) was carried out as in the preceding examples. The reaction product did not crystallize even at -70°, and it was therefore dissolved in petroleum ether and chromatographed on aluminum oxide (1 g, length of column 6 cm). Only 5 mg of crystals, m.p. 78-80° (from a mixture of petroleum ether and benzene) could be obtained as a result of successive elution with petroleum ether, a mixture of petroleum ether and benzene, and benzene. The dinitrophenylhydrazone formed fine yellow needles, m.p. 198-201° (decomposition).

Hydrogenation of the Diketones XVII A, XVII B, and XVII C in Presence of an Adams Platinum Catalyst

The diketones XVII A, XVII B, and XVII C did not undergo hydrogenation in alcoholic solution in presence of an Adams platinum catalyst. When attempts were made to hydrogenate these diketones in acetic acid (60-100 mg of diketone, 15-20 mg of PtO_2 and 5 ml of acetic acid; 3 hours), the original diketone (20-30 mg) was in every case recovered unchanged.

SUMMARY

1. Total syntheses of steroid diketones of the cis-cis series have been performed by the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and of 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2,4-dimethyl-2-cyclopenten-1-one (III). In both cases a total yield of about 60% was obtained of a mixture of three or four isomeric steroid diketones having the A and B rings and the C and D rings united in the cis-configuration.

2. It has been shown that, irrespective of the presence and positions of substituents in the A ring, all steroid diketones synthesized by the diene-condensation method have the so-called "inverted" structure, i.e. the D ring has an angular methyl group in the 14-position and a carbonyl group in the 15-position. For some compounds the difference between the isomers lies in the difference in relative spatial positions of the A and B rings and of the C and D rings; and for other compounds it lies in the difference in the spatial disposition of the hydrogen at C-8.

3. It has been shown that the 9(11) double bond in tetracyclic steroid diketones migrates comparatively readily to the 8(9)-position under the action of hydrochloric acid.

4. It has been found that the keto group in the D ring is extremely stable under the conditions of Clemmensen reduction, tetracyclic steroid 2,15- and 3,15-diketones being converted into 15-monoketones.

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SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XIX. CONDENSATION OF

3,4,4a,7,8,8a-HEXAHYDRO-4a-METHYL-5-VINYL-2(1H)-NAPHTHALENONE

AND 3,4,4a,5,6,8a-HEXAHYDRO-8a-METHYL-8-VINYL-2(1H)-NAPHTHALENONE

WITH 2-CYCLOHEXEN-1-ONES AND WITH CITRACONIC ANHYDRIDE

I. N. Nazarov, I. I. Zaretskaya, G. P. Verkholetova, and I. V. Torgov

In the preceding communication [1] we have described the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2,4-dimethyl-2-cyclopenten-1-one. By this means we obtained a number of steroid diketones of the cis-cis series and having an "inverted" structure:
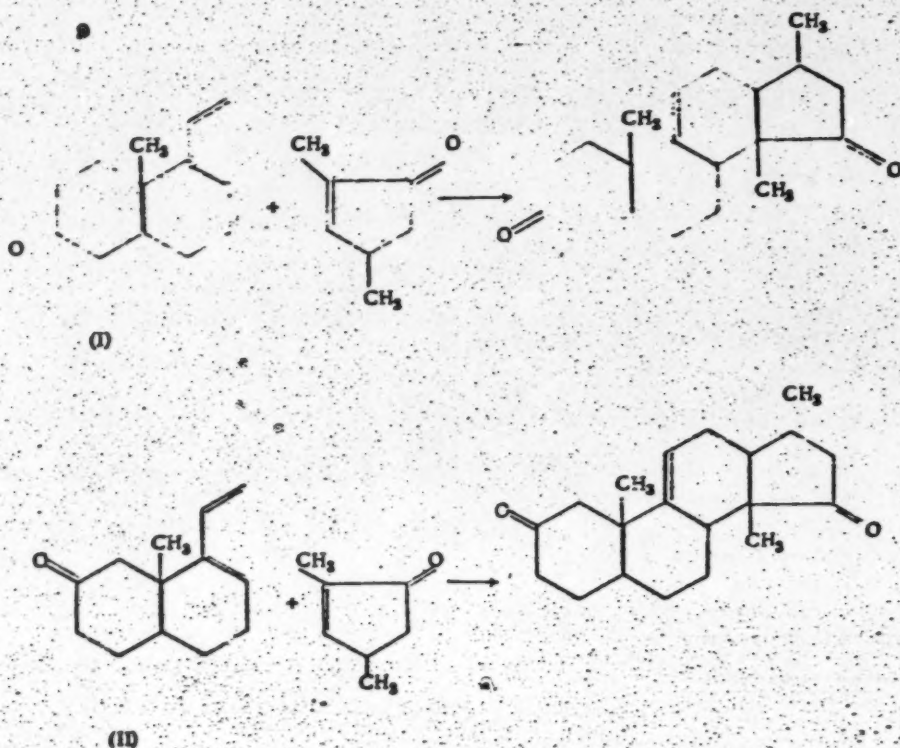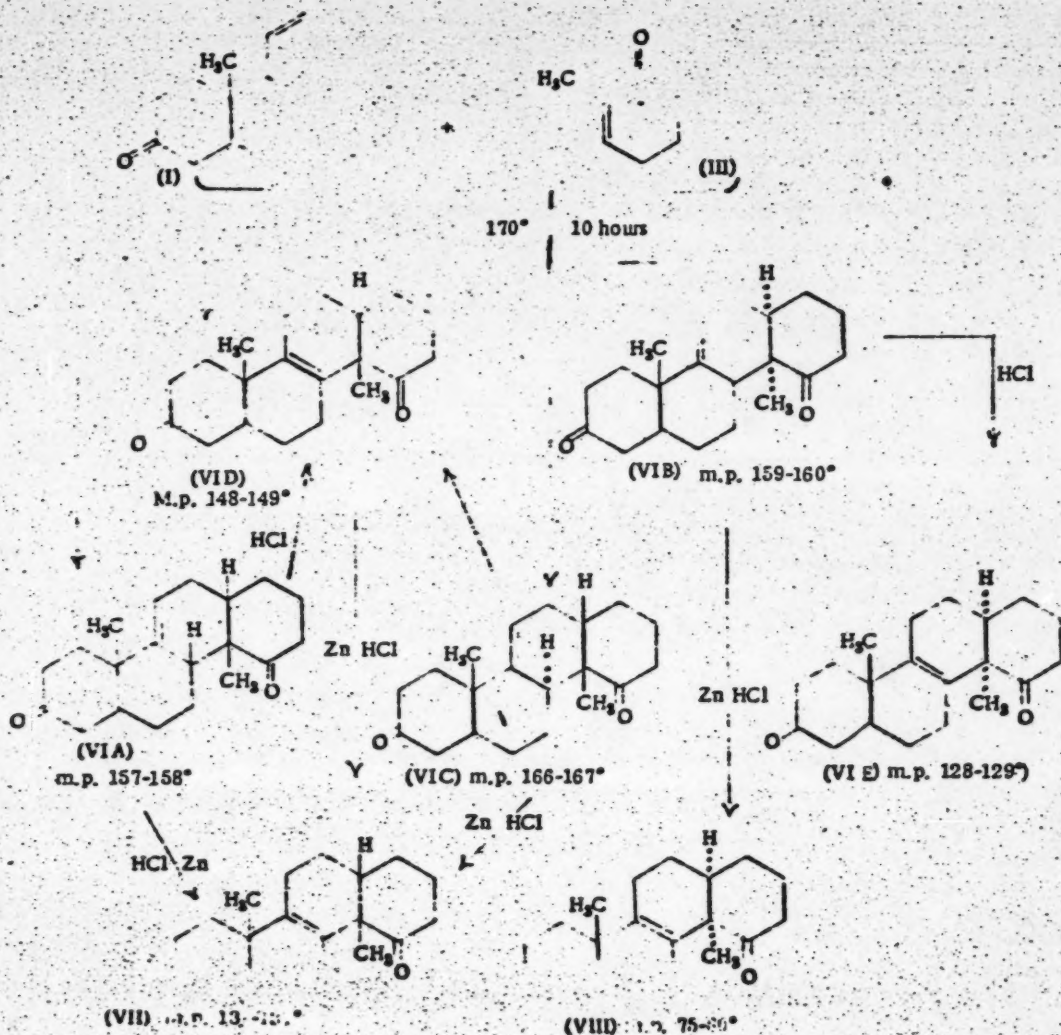

In the present investigation we have studied the condensation of the dienone I with 2-methyl-2-cyclohexen-1-one (III), with 2-cyclohexen-1-one (IV), with citraconic anhydride (V), and with p-benzoquinone, and also the condensation of the dienone II with 2-methyl-2-cyclohexen-1-one (III). When the dienone I was heated with ten times its amount of 2-methyl-2-cyclohexen-1-one (III) at 170° for ten hours, a 50% yield was obtained of a mixture of tetracyclic diketones of the cis-cis series, from which four isomers, VI A, VI B, VI C, and VI D, of 10,14-dimethylcardochrysanene 3,15-dione* were isolated in the proportions 40 : 10 : 5 : 1, approximately. In some

* Nazarov's nomenclature for synthetic steroids, see Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 4, 726 (Consultants Bureau Translation, p 651).

experiment the proportion of the isomer VI D was considerably more, and that of the isomer VI A was corresponding-ly less.

The difference between the isomers VI A and VI C lies in a difference in spatial disposition of the hydrogen atom at C-8, for, on being heated with hydrochloric acid, both isomers give the same isomer (VI D) with displacement of the double bond from the 9(11)- to the 8(9)-position, as shown in the preceding communication [1].

All three diketones, VI A, VI C, and VI D, give the same monoketone (VII) when subjected to Clemmensen reduction. Since it has been shown previously [1] that it is the keto group in the A ring that is removed in this reaction, the monoketone obtained must have the structure 10,14-dimethyl-8-cardochrysanene-15-one (VII). Reduction of the isomer VI B yields the monoketone VIII, which is distinct from the monoketone VII. If it is assumed, on analogy with the already studied reactions of the dienone I with 2-4-dimethyl-2-cyclopenten-1-one [1], that all of the isomers are of inverted structure, then the difference between the isomers VI B and VI A can only be explained by a difference in the spatial arrangement of the substituents at $C_{13}-C_{14}$.

(I)

(III)

170°   10 hours

(VID) M.p. 148-149°

(VIB) m.p. 159-160°

HCl

(VIA) m.p. 157-158°

Zn HCl

(VIC) m.p. 166-167°

Zn HCl

(VI E) m.p. 128-129°)

HCl Zn

Zn HCl

(VII) m.p. 13-...°

(VIII) m.p. 75-...°

The fact that the isomer VI D is present in the reaction mixture shows that in the course of the diene synthesis the double bond is displaced from its original 9(11)-position to the 8(9)-position.

Such instances of the displacement of a double bond in the course of the diene synthesis are comparatively rare. In the condensation, however, of a sorbic or muconic ester with maleic anhydride, the double bond moves

to the position of conjugation with the carboxyl [2]:

R = CH₃, CO₂C₂H₅

R = CH$_3$, CO$_2$C$_2$H$_5$
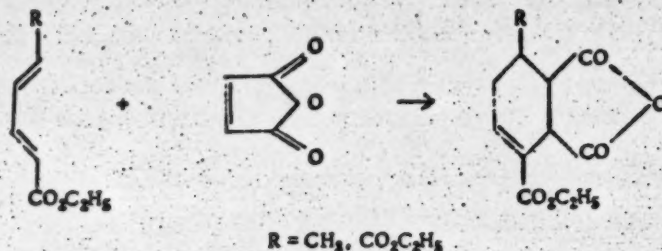
In the condensation, also, of 1,4-diphenyl-1,3-butadiene with maleic anhydride, a mixture of readily inter-convertible isomers is obtained, and this is explained by the investigators as a displacement of the double bond [3]:
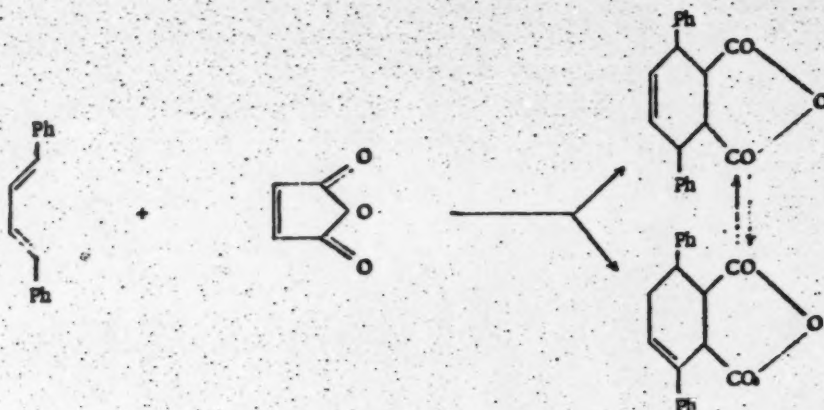
Similar phenomena in sorbic acid condensations have been observed also by Deno [4] and Alder [5]. We consider that the isomer VI D, being the most stable one, has an 8(9) double bond, whereas in the isomer VI A, which is formed in the greatest amount during the diene synthesis, the double bond is in the 9(11)-position.

The carbonyl group of the monoketone VII is exceptionally inert: it will not undergo Clemmensen reduction, and it does not react with methylmagnesium iodide or methyllithium, even after prolonged heating. This behavior is probably to be explained by steric hindrance due to the powerful screening effect of the 14-methyl group, and this indirectly confirms the correctness of our assumed "inverted" structure for the ketone VII and therefore the structure of the diketones VI A, VI C, and VI D.

Condensation of 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-methyl-2-cyclo-hexen-1-one (III) also gave a mixture of ketones, from which it was found possible to isolate three isomers, IX A, IX B, and IX C, of 10,14-dimethyl-9-cardochrysanene-2,15-dione in the proportions of 15 : 12 : 1 approximately.

(II)

(III)

(IX A, B, C)

(IX A), m p. 143-144°
(IX B), m. p. 203-205°
(IX C), m. p. 182-183°

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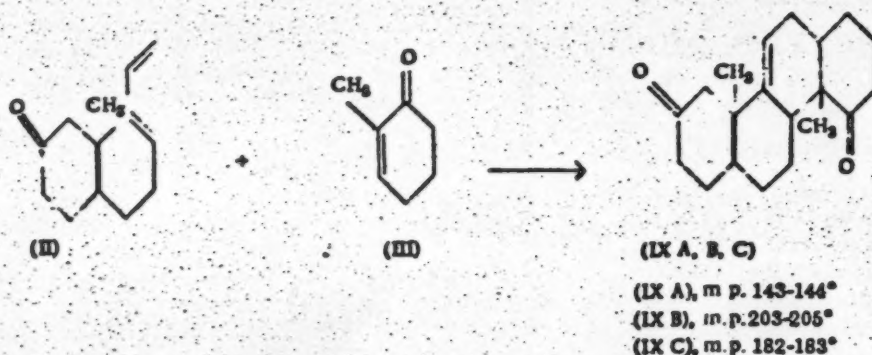
Owing to the small amount available of the original dienone (II) and the small amounts obtained of the diketones IX, the latter were not investigated further.

The condensation of the dienone I with 2-cyclohexen-1-one (IV) was complicated by the great tendency of the latter to condense with itself. The best results (27% yield on the amount of dienone that reacted) were obtained by heating the components at 150° for ten hours, when two isomers, X A and X B, of 10-methyl-9-cardochrysanene-3,15-dione were obtained in the ratio of 6 : 1 approximately.

Condensation of the dienone I with benzoquinone went very readily, even at 60°, and gave a mixture of products, from which it was found possible to isolate one isomer of 10-methyl-9,16-cardochrysadiene-3,15,17a-trione (XI). Heating of the dienone I with citraconic anhydride (V) at 100° gave a mixture of anhydrides, from which a pure product of structure XII or XII A was isolated.

(XI) m.p. 185-186°

(IV) 150°

(XA) m.p. 150-151°
(XB) m.p. 181-183°

(I)

60°

(V) 100°

(XII) m.p. 175-176

(XIIA)

Al(OC₃H₇iso)₃

(XIII)

(XIV)

We have also reduced the dienone I with aluminum isopropoxide to the dienol XIII (a mixture, of course, of stereoisomers). This dienol (XIII) was condensed with 2,4-dimethyl-2-cyclopenten-1-one and with p-benzoquinone. In the first case no crystalline product could be isolated, and in the second case 10-methyl-9,16-cardochrysadien-3-ol-15,17a-dione (XIV) was obtained in low yield.

EXPERIMENTAL

3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) (b.p. 100-103° at 1 mm; n_D^{20} 1.5260) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) (b.p. 106-107° at 1.5 mm; n_D^{20} 1.5270) were previously described by us [2]. 2-Methyl-2-cyclohexen-1-one (III) (b.p. 56° at 9 mm; n_D^{20} 1.4865) and 2-cyclohexenone (IV) (b.p. 63° at 20 mm; n_D^{20} 1.4872) were prepared by the method developed in our laboratory [7]. Citraconic anhydride (V) (b.p. 80° at 7 mm; n_D^{20} 1.4720) was prepared by Shriner's method [8].

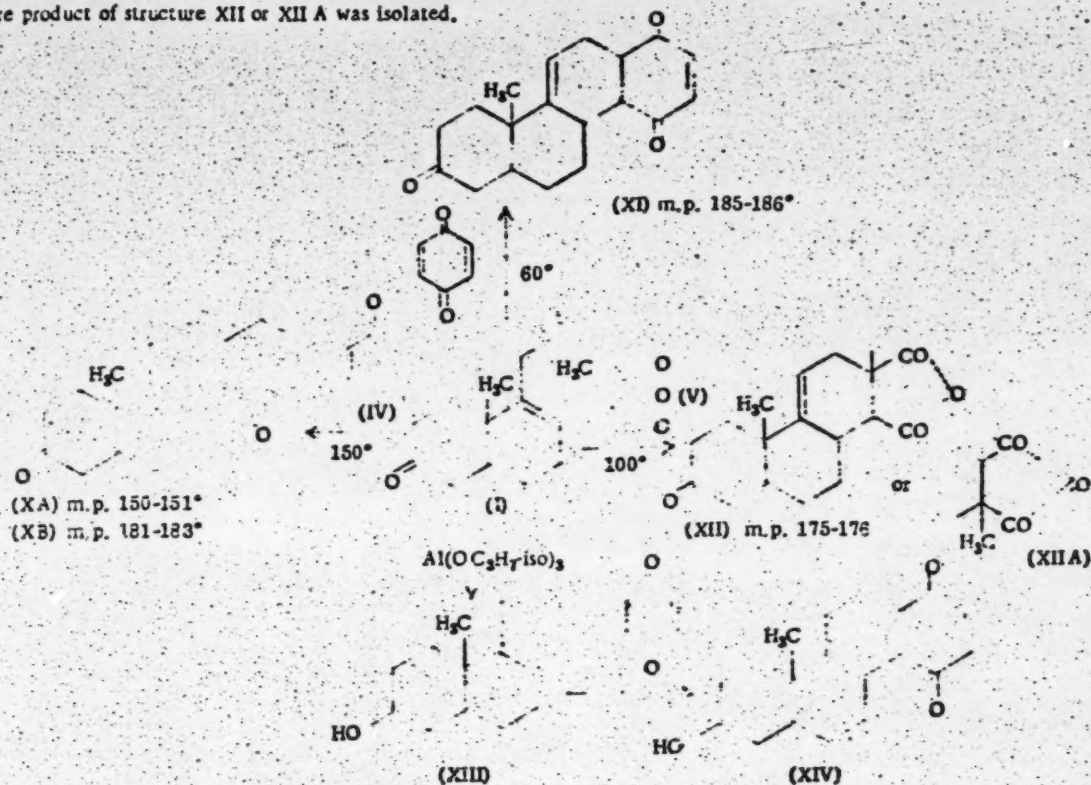### Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-Methyl-2-cyclohexen-1-one (III)

A mixture of 12 g of the dienone I, 120 g of 2-methyl-2-cyclohexen-1-one, and 0.1 g of pyrogallol was heated in glass tubes in a carbon dioxide atmosphere for ten hours at 170-175°. Unchanged methylcyclohexenone (114 g)

and dienone (4.5 g) were distilled off under reduced pressure, and the residue was dissolved with heat in 15 ml of petroleum ether. Crystallization rapidly set in, yielding 4.5 g of a crystalline mixture, m.p. 124-150°. After three days a further 1.05 g of mixture had separated from the mother liquor. The unchanged dienone was again treated with methylcyclohexenone under the same conditions, and 0.8 g of the crystalline mixture and 2.75 g of the dienone I were isolated.

Distillation of the mother liquors from the two experiments at 0.5 mm yielded 5.9 g of a viscous liquid, b.p. 160-170°, and this partially crystallized out when diluted with petroleum ether, yielding 1.4 g of crystals. The total amount of crystals obtained was 7.95 g, i.e., 42% on the total amount of dienone I taken, and 55% on the amount that reacted. The isomers were separated by fractional crystallization from a mixture of petroleum ether and benzene:

Isomer VI A, m.p. 157-158°, 1.2 g.

| | | Found %: | C 79.95; 79.7; H 9.4; 9.3 |
| $C_{20}H_{28}O_2$ | Calculated %: | C 80.0 | H 9.4 |

Isomer VI B, m.p. 159-160°, 0.35 g.

| | | Found %: | C 80.0; 80.05; H 9.4; 9.35 |
| $C_{20}H_{28}O_2$ | Calculated %: | C 80.0; | H 9.4 |

A mixture of VI A and VI B melted at 130-138°.

Isomer VI C, m.p. 166-167°, 0.17 g.

| | | Found %: | C 80.0; 79.9; H 9.3; 9.4 |
| $C_{20}H_{28}O_2$ | Calculated %: | C 80.0; | H 9.4 |

A mixture with VI A melted at 130-140°, and with VI B at 130-140°.

Isomer VI D, m.p. 148-149°, 30 mg.

| | | Found %: | C 79.9; 80.1; H 9.6; 9.5 |
| $C_{20}H_{28}O_2$ | Calculated %: | C 80.0; | H 9.4 |

Mixtures with VI A and with VI B melted at 125-130°.

Attempt to Effect the Thermal Isomerization of the Diketones VI A — D

Samples of the diketones were heated in capillaries at 200° for one hour. The substances were greatly resinified, and on cooling only the isomer VI D partially crystallized. The crystals melted at 146-147°, i.e., the isomer VI D had not undergone thermal isomerization.

Isomerization of the Diketone VI A

A mixture of 110 mg of the diketone VI A, m.p. 157-158°, 3 ml of acetic acid, 3 ml of concentrated hydrochloric acid, and 5 ml of toluene was heated under reflux for nine hours. The toluene layer was separated, neutralized by agitation with 4% caustic soda, and filtered. The solvents were distilled off under reduced pressure, and the residue was crystallized from a mixture of benzene and petroleum ether (1 : 4), yielding 86 mg of the diketone VI D, m.p. 146-147°. A mixture melting point with the diketone VI D isolated after the condensation reaction was not depressed.

Isomerization of the Diketone VI C

The isomerization of the diketone VI C was performed similarly: from 35 mg of VI C, m.p. 166-167°, 5 mg of the diketone VI D, m.p. 145-146°, was obtained. In admixture with samples of the diketone VI D obtained above, there was no depression of melting point.

Isomerization of the Diketone VI B

The isomerization was performed in a similar manner: from 65 mg of the diketone VI B, m.p. 159-160°, 10 mg of the diketone VI E, m.p. 128-129° (from alcohol), was obtained.

| | | Found %: | C 79.5; 79.7; H 9.3; 9.5 |
| $C_{20}H_{28}O_2$ | Calculated %: | C 80.0; | H 9.4 |

Attempt to Effect the Isomerization of the Diketone VI D

The isomerization treatment was carried out similarly on the diketone VI D: from 60 mg of the diketone VI D, m.p. 148-149°, 45 mg of the original diketone, m.p. 146-147°, was obtained after the usual treatment. The mixture melting point test showed no depression.

Clemmensen Reduction of the Diketone VI A

A mixture of 500 mg of the diketone VI A, m.p. 157-158°, 5 ml of toluene, 6 ml of acetic acid, 6 ml of concentrated hydrochloric acid, and 2.5 g of amalgamated zinc was boiled under reflux for four hours. The toluene layer was separated, neutralized by agitation with a 10% solution of caustic soda, and filtered. The solvent was removed under reduced pressure, and the solid residue was crystallized from petroleum ether, yielding 303 mg (63%) of the monoketone VII as colorless plates, m.p. 136-137°.

$$C_{22}H_{34}O. \quad \begin{array}{ll} \text{Found \%:} & \text{C 84.0; 83.9; H 10.6; 10.6} \\ \text{Calculated \%:} & \text{C 83.85;} \quad \text{H 10.6} \end{array}$$

Clemmensen Reduction of the Diketone VI C

The reduction was performed in a similar manner: from 26 mg of the diketone, m.p. 166-167°, 7 mg of the ketone VII, m.p. 135-136° was obtained. In admixture with the sample of ketone obtained in the previous experiment it showed no melting point depression.

Clemmensen Reduction of the Diketone VI D

The reduction was performed in a similar manner: from 200 mg of the diketone VI D, m.p. 148-149°, 106 mg of the ketone VII, m.p. 135-136°, was obtained. In admixture with samples of ketones from the preceding experiments there was no depression in melting point.

Clemmensen Reduction of the Diketone VI B

The reduction was performed in a similar manner: from 250 mg of the diketone VI B, m.p. 159-160°, after the usual treatment and one crystallization, 130 mg of a substance of m.p. 70-80° was obtained. Recrystallization gave 75 mg of the ketone VIII, m.p. 75-80°. Further crystallizations did not raise the melting point and did not make the melting range any narrower.

$$C_{22}H_{34}O. \quad \begin{array}{ll} \text{Found \%:} & \text{C 84.8; H 10.7} \\ \text{Calculated \%:} & \text{C 83.85; H 10.6} \end{array}$$

The high carbon content indicates that the ketone was contaminated by a hydrocarbon which could not be separated by crystallization.

Action of Methylmagnesium Bromide and Methyllithium on the Ketone VII

A solution of 230 mg of the ketone VII, m.p. 136-137°, in a mixture of 6 ml of ether and 1 ml of benzene was added to a Grignard reagent prepared from 0.2 g of magnesium, 1.2 g of methyl iodide, and 10 ml of ether. The reaction mixture was boiled for 15 minutes, cooled, and decomposed with ice. The ether layer was separated, the ether was removed, and the residue was crystallized from ether, yielding 150 mg of unchanged ketone VII, m.p. 136-137°. A mixture melting point with the original ketone was not depressed. When the reaction was carried out at 100° in toluene, 30 mg of the ketone VII was recovered from 170 mg taken, and the residue was a noncrystallizing mass. Similar results were obtained when methyllithium was used.

Condensation of 3,4,4a,5,6,8a-Hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II)

with 2-Methyl-2-cyclohexen-1-one (III)

A mixture of 2.0 g of the dienone II and 5 g of 2-methyl-2-cyclohexen-1-one (III) was heated in a carbon dioxide atmosphere in a sealed glass tube for 13 hours at 170-175°. Methylcyclohexenone (4.1 g) was distilled off, and the residue was diluted with twice its volume of methanol and set aside to crystallize. After one week the crystals that had formed (0.3 g; m.p. 135-155°) were separated mechanically into a low-melting (141-143°) fraction and a high-melting (178-179°) fraction. After standing for two days the mother liquor yielded a second crop of crystals (0.2 g), m.p. 194-199°. Three isomers were isolated by crystallization from methanol.

Isomer IX A, prisms of m.p. 143-144° (corr.), 130 mg.

$$C_{22}H_{30}O_2 \quad \begin{array}{ll} \text{Found \%:} & \text{C 79.8; 79.7; H 9.5; 9.4} \\ \text{Calculated \%:} & \text{C 80.0;} \quad \text{H 9.4} \end{array}$$

Isomer IX B, fine plates of m.p. 203-205° (corr.), 100 mg.

Found %:   C 79.9; 79.7; H 9.4; 9.65

$C_{20}H_{28}O_2$ Calculated %: C 80.0;   H 9.4

Isomer IX C, needles of m.p. 182-183°, 8 mg.

Found %:   C 79.6; 79.7; H 9.4; 9.3

$C_{20}H_{28}O_2$ Calculated %: C 80.0;   H 9.4

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I)

with 2-Cyclohexen-1-one (IV)

A mixture of 5.5 g of the dienone I, 40 g of 2-cyclohexen-1-one (IV), and 40 mg of pyrogallol was heated in an atmosphere of carbon dioxide in a sealed glass tube at 150° for ten hours. Unchanged cyclohexenone (35.5 g) and dienone (1.6 g) were distilled off, and the residue was mixed with 8 ml of petroleum ether and set aside for one day to crystallize. A crystalline mixture of m.p. 137-145° was obtained. The yield was 1.05 g, i.e., 17% on the total amount of dienone taken, or 27% on the amount that reacted. Two isomers, X A and X B, were isolated by means of crystallization from a mixture of petroleum ether and benzene (5 : 1).

Isomer X A, plates of m.p. 150-151°, 0.3 g.

Found %:   C 79.6; 79.7; H 9.1; 9.2

$C_{19}H_{26}O_2$ Calculated %: C 79.7;   H 9.1

Isomer X B, needles of m.p. 181-183°, 50 mg.

Found %:   C 79.4; 79.4; H 9.3; 9.3

$C_{19}H_{26}O_2$ Calculated %: C 79.7;   H 9.1

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I)

with p-Benzoquinone

A solution of 1 g of the dienone I and 0.55 g of benzoquinone, m.p. 115°, in 10 ml of absolute dioxane was heated in a carbon dioxide atmosphere in a glass tube at 60° for 4 hours 30 minutes. The dioxane was removed, and the residue was diluted with 6 ml of petroleum ether and 1 ml of benzene. The solution yielded 0.85 g (55%) of a mixture of crystals, and recrystallization from a mixture of petroleum ether and benzene yielded 0.12 g of pure triketone (XI) in the form of large yellowish scales, m.p. 185-186°.

Found %:   C 76.2; 76.5; H 7.5; 7.6

$C_{19}H_{22}O_3$ Calculated %: C 76.5;   H 7.4

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I)

with Citraconic Anhydride (V)

A solution of 1.9 g of the dienone I and 1.1 g of citraconic anhydride (V) in 5 ml of benzene was heated in a carbon dioxide atmosphere in presence of traces of Methylene Blue in a glass tube at 100° for six hours. Benzene was removed under reduced pressure, and the viscous mass that remained partially crystallized when ether was added thus yielding 0.91 g of a crystalline mixture. The mixture was boiled with 20 ml of petroleum ether, and the undissolved crystals were separated and washed with petroleum ether. The product was 140 mg of the tricyclic anhydride XII or XII A, m.p. 175-176°.

Found %:   C 71.6; 71.75; H 7.3; 7.3

$C_{18}H_{22}O_4$ Calculated %: C 71.5;   H 7.3

Crystals of m.p. 150-160° separated from the mother liquor; these consisted of a mixture of isomers, and it was not found possible to separate them.

Reduction of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) to

1,2,3,4,4a,7,8,8a-Octahydro-4a-methyl-5-vinyl-2-naphthol (XIII)

A mixture of 5.2 g of the dienone I and 50 ml of a molar solution of distilled aluminum isopropoxide in isopropyl alcohol was distilled from a flask fitted with an efficient column so that distillation was at 6-8 drops per

minute. After three hours' boiling, the distillate no longer gave a test for acetone (with dinitrophenylhydrazine). Boiling was continued for a further 30 minutes, and the bulk of the isopropyl alcohol was then distilled off under reduced pressure. The viscous mass that remained was decomposed by addition, under cooling, of 90 ml of 6% hydrochloric acid, and it was then extracted three times with ether. The ether extract, on standing, yielded 0.3 g of crystals, m.p. 133-200°. Crystallization from benzene gave a substance of m.p. 208-209°, corresponding to the formula $C_{13}H_{22}O_2$.

$$\text{Found \%: } C\ 73.9;\ H\ 11.1$$
$$C_{13}H_{22}O_2 \qquad \text{Calculated \%: } C\ 74.3;\ H\ 10.5$$

When the ether was removed, a viscous mass remained, and this, after dilution with 4 ml of petroleum ether and cooling, yielded 0.5 g of crystals, m.p. 155-157°. Crystallization from a mixture of petroleum ether and benzene (1 : 4) gave a substance of m.p. 160-161°, also of formula $C_{13}H_{22}O_2$.

$$\text{Found \%: } C\ 74.3;\ H\ 10.4$$
$$C_{13}H_{22}O_2 \qquad \text{Calculated \%: } C\ 74.3;\ H\ 10.5$$

The structures of these two crystalline compounds have not been established.

The filtrate obtained after separation of the crystals was vacuum-distilled, and yielded 3 g (50%) of 1,2,3,4,-4a,7,8,8a-octahydro-4a-methyl-5-vinyl-2-naphthol (XIII) as a viscous liquid, b.p. 120-121.5° at 1.5 mm, n_D^{20} 1.5293.

$$\text{Found \%: } C\ 80.4;\ 80.5;\ H\ 10.6;\ 10.55$$
$$C_{13}H_{20}O. \qquad \text{Calculated \%: } C\ 81.2; \qquad H\ 10.5$$

Condensation of 1,2,3,4,4a,7,8,8a-Octahydro-4a-methyl-5-vinyl-2-naphthol (XIII) with p-Benzoquinone

A solution of 0.8 g of the dienol XIII and 0.45 g of benzoquinone in 8 ml of dioxane was heated in a carbon dioxide atmosphere in a glass tube for five hours at 60°. The dioxane was removed under reduced pressure, and the residue was diluted with petroleum ether, when it partially crystallized, yielding 0.40 g (32%) of crystals of m.p. 128-130°. Two crystallizations from benzene gave the pure hydroxy diketone (XIV), m.p. 130-131°.

$$\text{Found \%: } C\ 76.0;\ 76.0;\ H\ 8.0;\ 8.1$$
$$C_{19}H_{24}O_3 \qquad \text{Calculated \%: } C\ 76.0; \qquad H\ 8.05$$

Condensation of the dienol XIII with 2,4-dimethyl-2-cyclopenten-1-one at 170° and at 140° gave noncrystallizing mixtures of products. It was not found possible to resolve them by chromatography.

SUMMARY

1. The total syntheses of some D-homosteroid diketones of the cis-cis series having a 15-keto group have been effected by condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-methyl-2-cyclohexen-1-one (III). Four isomeric tetracyclic ketones have been isolated, and of these two, VI A and VI C, differ only in the spatial disposition of the hydrogen at C_8, the third, VI D, differs in the position of the double bond (8- instead of 9-), and the fourth (VI B) differs from the other three in the spatial arrangement of the substituents at C_{13}-C_{14}.

2. It has been shown that in the course of the diene condensation the double bond may be displaced from the 8(11)- to the 8(9)-position.

3. When the steroid diketones are subjected to Clemmensen reduction, only the keto group in the ring A is removed, and the diketone is converted into a 15-monoketone.

4. Condensation of 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-methyl-2-cyclohexen-1-one (III) yielded three isomeric steroid diketones, IX A, IX B, and IX C. Condensations of 3,4,4a,-7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-cyclohexen-1-one, p-benzoquinone, and citraconic anhydride have also been carried out, and the compounds X, XI, and XII have been obtained.

5. Reduction of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with aluminum isopropoxide yielded 1,2,3,4,4a,7,8,8a-octahydro-4a-methyl-5-vinyl-2-naphthol (XIII), which, on being condensed with

p-benzoquinone, yielded the tetracyclic hydroxy diketone XIV.

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SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XX. CONDENSATION

OF 3,4,4a,7,8,8a-HEXAHYDRO-4a-METHYL-5-VINYL-2(1H)-NAPHTHALENONE

AND 3,4,4a,5,6,8a-HEXAHYDRO-8a-METHYL-8-VINYL-2(1H)-NAPHTHALENONE

WITH 2-CYCLOPENTEN-1-ONE, 2-METHYL-2-CYCLOPENTEN-1-ONE,

AND 3,5-DIMETHYL-3-CYCLOPENTENE-1,2-DIONE

I. N. Nazarov, G. P. Verkholetova, I. V. Torgov,
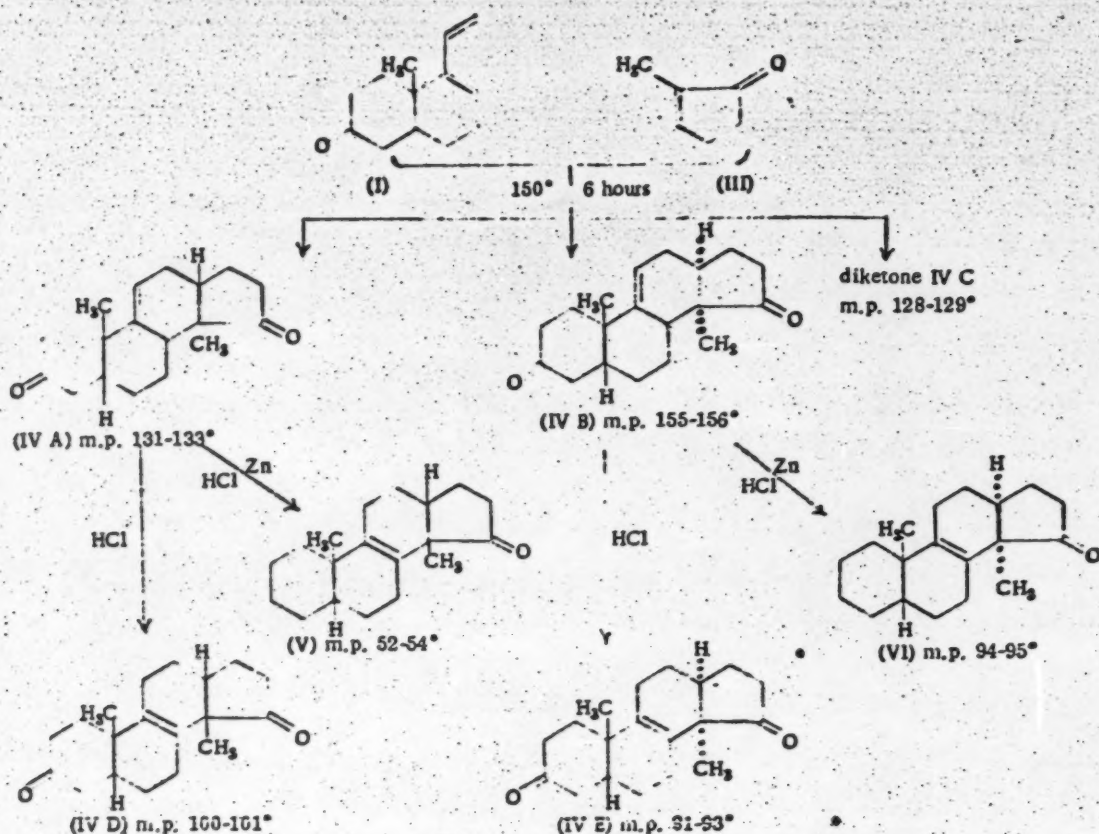
I. I. Zaretskaya, and S. N. Ananchenko

In the preceding communications [1, 2] we have described the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with various α,β-unsaturated cyclic ketones. As a result we have obtained a number of tetracyclic diketones of the cis-cis series, which have the fundamental skeleton of natural steroids, but have in most cases the so-called "inverted" structure:
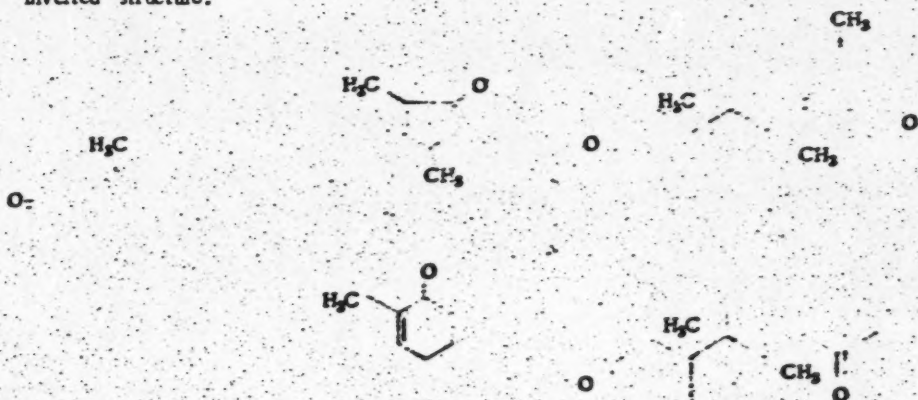
Particular interest is presented by the synthesis of steroid diketones having a cyclopentane D ring (and no methyl group in the 17-position), since they are closest in composition and structure to natural hormones. In the present investigation, therefore, we have studied the condensation of dienones I and II with 2-methyl-2-cyclopenten-1-one (III), and have established the structures of the isomeric steroid diketones so obtained. It was found that in both cases the main products were again of the "inverted" structure.

The condensation of the dienones I and II with 2-methyl-2-cyclopenten-1-one did not go as well (30-35% yield) as the previously described condensation of these dienones with 2,4-dimethyl-2-cyclopenten-1-one (50-60% yield). The yield was reduced as a result of the high tendency of 2-methyl-2-cyclopenten-2-one to undergo self-condensation. Thus, when it is heated at 170° for three hours, it is completely converted into a viscous mixture of polymeric products, whereas 2,4-dimethyl-2-cyclopenten-1-one is practically unaffected under these conditions. The best results were obtained by heating the dienone I with double its quantity of 2-methyl-2-cyclopenten-1-one (III) at 150° for six hours. A 30% yield was then obtained of a mixture of tetracyclic diketones, from which three

isomers, IV A, IV B, and IV C, of 10-14-dimethyl-9-cardosterene-3,15-dione * were isolated, the last in an impure state. The first two isomers, as will be shown below, were of the "inverted" structure. We therefore have the same picture as in the condensation of the dienone I with 2,4-dimethyl-2-cyclopenten-1-one, in which three isomers were also obtained, these having steroid skeletons with an inverted D ring.

(I)   150°   6 hours   (III)

diketone IV C
m.p. 128-129°

(IV A) m.p. 131-133°

(IV B) m.p. 155-156°

(V) m.p. 52-54°

(VI) m.p. 94-95°

(IV D) m.p. 100-101°

(IV E) m.p. 51-53°

The isomers IV A and IV B differ in spatial configuration, since they give different monoketones V and VI when subjected to Clemmensen reduction. There can be no doubt that the difference between these ketones, and also between the original ketones IV A and IV B, lies in the spatial arrangement of substituents at $C_{13}-C_{14}$, as indicated in the formulas given.

When the diketone IV A or IV B is boiled with hydrochloric and acetic acids, it is isomerized with displacement of the double bond into the diketone IV D or IV E respectively. Such isomerization can be explained only by the displacement of the double bond from the 9(11)-position to the 8(9)-position, as has been shown previously on the basis of many examples [1, 2].

The establishment of the structure of the ketones V and VI presented great difficulties. The method of oxidation with iodine in an alkaline medium with subsequent dehydrogenation of the acid formed into a phenanthrene derivative, which has given a positive result in other cases [1], was unsuitable in this case, since both possible structures, "normal" and "inverted", would give the same product, 1,2-dimethylphenanthrene. It appeared to be possible to convert the ketone V or VI into the corresponding alcohol by the action of methylmagnesium bromide, and

* Nazarov's nomenclature for synthetic steroids; see Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 726 (Consultants Bureau Translation, p 651).

then to convert the alcohol by dehydration, hydrogenation, and dehydrogenation into a 16,17-dihydromethylcyclopenta[a]phenanthrene described in the literature:
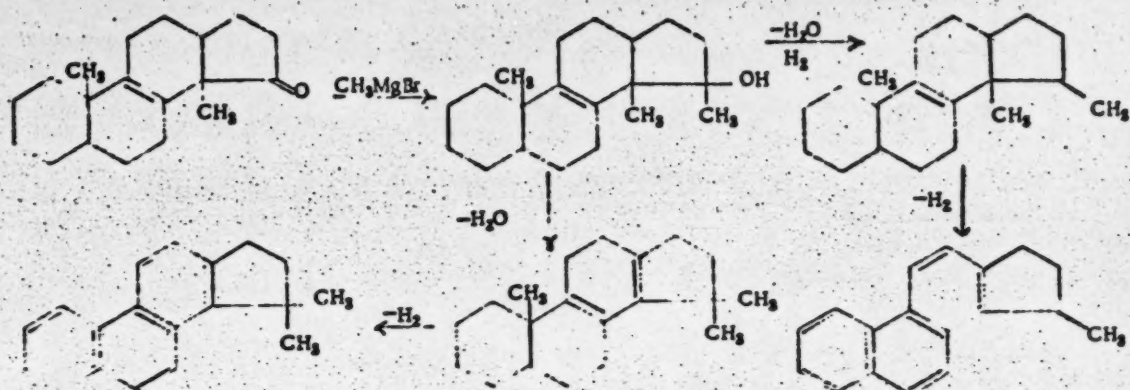
This method, however, was subject to doubt for two reasons. In the first place, the keto group in the D ring is very inert to the Grignard reagent, as we have shown in the preceding communication [2] in the case of a D-homosteroid diketone. In the second place, in the dehydration, a retro-pinacolin rearrangement may very well occur, which would lead to the unknown 16,17-dihydro-15,15-dimethylcyclopenta[a]phenanthrene. A similar example is found in the behavior of the methyl ether of estrone [3]:
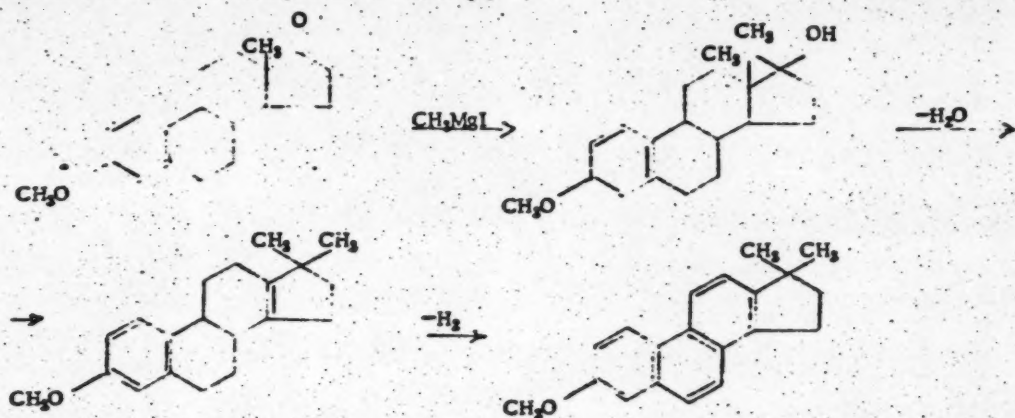
The following m thod also appeared to be possible for the determination of the structure of the steroid ketones V and VI:
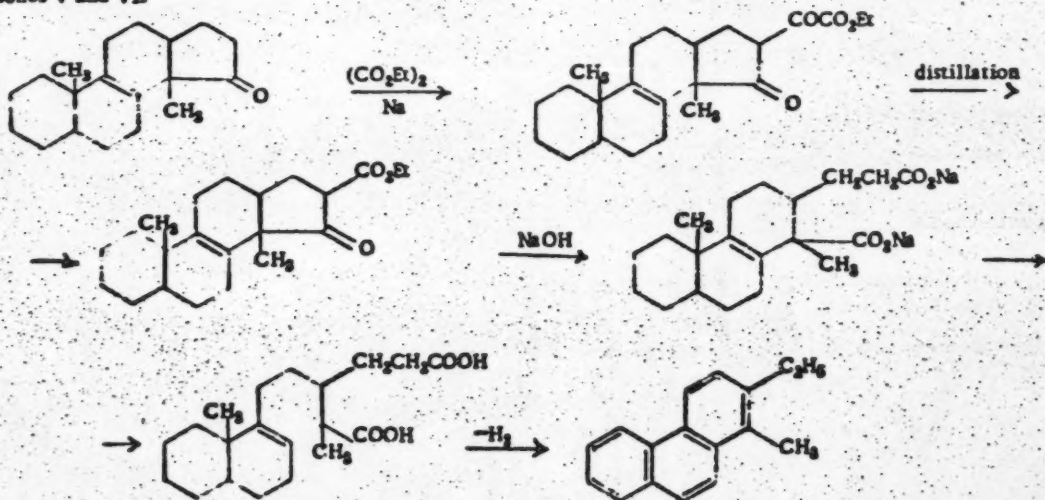
However, preliminary experiments on 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone, taken as a model example, showed that although condensation with oxalic ester proceeded readily, the elimination of carbon monoxide did not occur even at 200° (the behavior thus contrasting with that of the corresponding cyclohexane compounds):

The method of direct dehydrogenation of the ketones V and VI in presence of palladized charcoal was therefore adopted. This method has recently been successfully applied by Bachmann [4] for determining the structures of steroid compounds of the equilenin and estrone series:
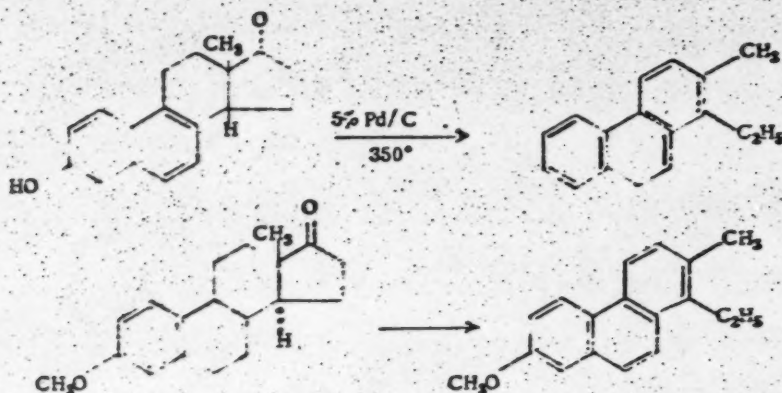
Dehydrogenation of the ketones V and VI gave, though in very low yield (less than 10%), some 2-ethyl-1-methylphenanthrene (VII) (in both cases), which was characterized both by a mixture melting point with an authentic sample, and also by its conversion into the corresponding quinone (VIII) and quinoxaline (IX):
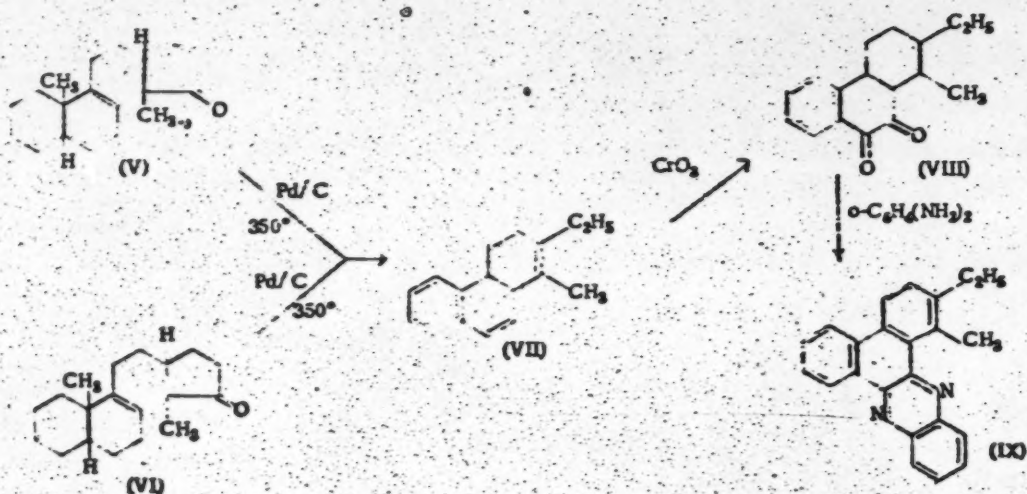
The higher yield (about 80%) of the hydrocarbon VII obtained by Bachmann is to be explained by the comparatively easy dehydrogenation of steroids having one or two aromatic rings.
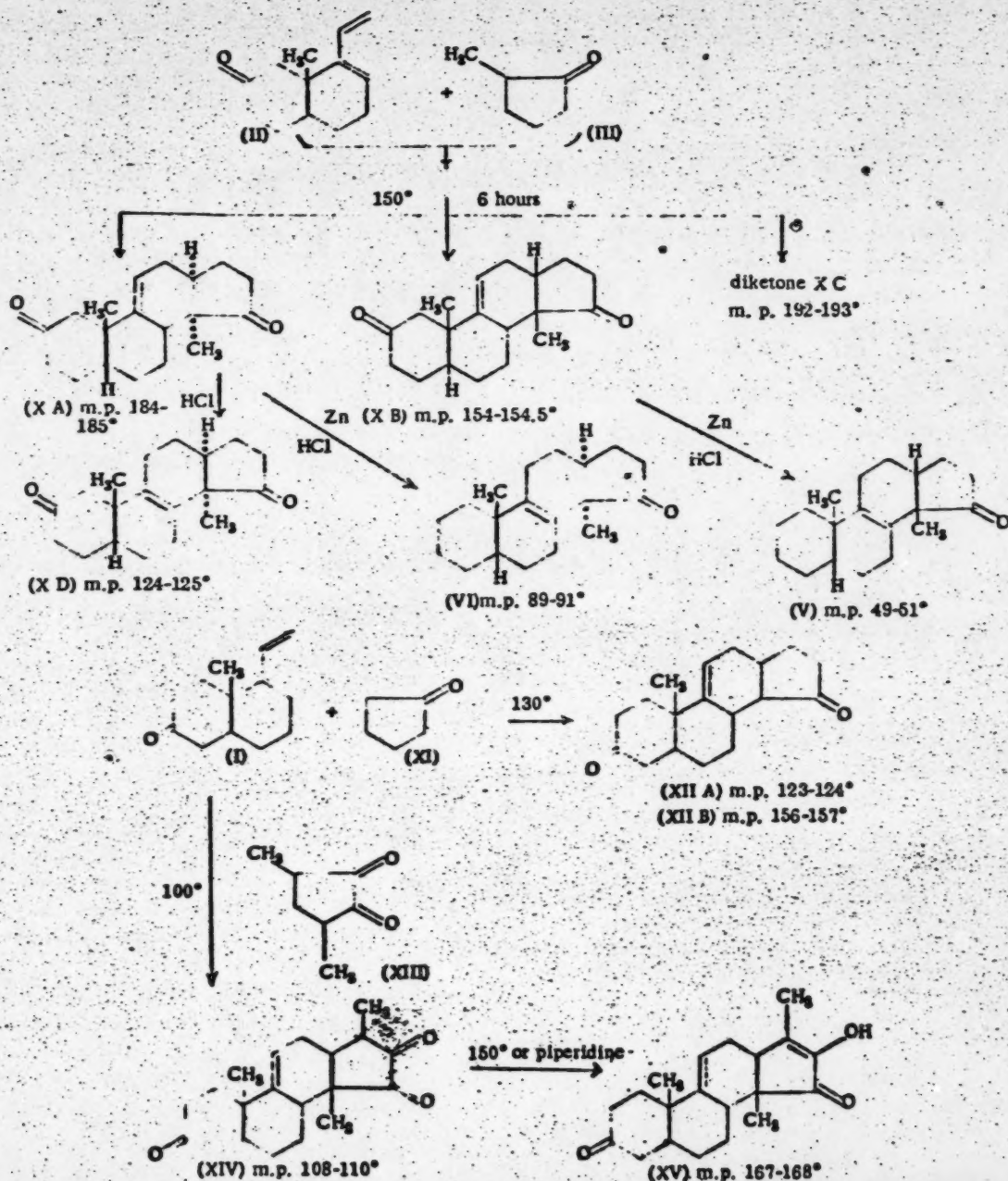
The isolation of 2-ethyl-1-methylphenanthrene (VII) from the dehydrogenation products proves beyond doubt that the diketones V and VI, and therefore also the original diketones IV A and IV B, are of "inverted" structure.

Condensation of the dienone II with 2-methyl-2-cyclopenten-1-one (III), carried out under the same conditions, gave a 38% yield of a mixture of three isomers, X A, X B, and X C, of 10-14-dimethyl-9-cardosterene-2,15-dione in the proportions of 25 : 7 : 1 approximately.

Clemmensen reduction of the diketone X A gave the ketone VI, and the diketone X B gave the ketone V, and in this way their structures were established. Owing to the smallness of the amount of the diketone X C obtained, its structure was not determined.

When boiled with hydrochloric and acetic acids, the diketone X A was isomerized to the diketone X D, with displacement of the double bond from the 9(11)- to the 8(9)-position.

We further carried out the condensation of the dienone I with 2-cyclopenten-1-one (XI), but, as the latter is still more sensitive to heating than 2-methyl-2-cyclopenten-1-one (III), it was necessary to lower the temperature to 130°. An 11% yield was obtained of a crystalline mixture of isomers, from which it was found possible to isolate two isomers, XII A and XII B, of 10-methyl-8-cardosterene-3,15-dione in the pure state.

(II) + (III)

150°   6 hours

diketone X C
m. p. 192-193°

(X A) m.p. 184-185°   HCl   Zn (X B) m.p. 154-154.5°   Zn HCl

(X D) m.p. 124-125°   HCl   (VI) m.p. 89-91°   (V) m.p. 49-51°

(I) + (XI)   130°   (XII A) m.p. 123-124°
(XII B) m.p. 156-157°

100°

(XIII)

(XIV) m.p. 108-110°   150° or piperidine   (XV) m.p. 167-168°

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When the dienone I was condensed with 3,5-dimethyl-3-cyclopentene-1,2-dione (X) at 100°, a 14% yield of 10,14,17-trimethyl-9-cardosterene-3,15,16-trione (XIV) was obtained. The latter, even by simple fusion, is very readily isomerized into 10,14,17-trimethyl-9,16-cardosteradien-16-ol-3,15-dione (XV), the enol form of the triketone XIV. The same transformation can be effected also by the action of piperidine. If the condensation of the dienone I with the diketone XIII is carried out at 120°, it is not possible to isolate any triketone XIV; only the hydroxy diketone XV is obtained. We have previously observed similar cases of the ready isomerization of cyclic 1,2-diones into enolones [5].

EXPERIMENTAL

3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) (b.p. 100-103° at 1 mm; n_D^{20} 1.5260) and 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) (b.p. 106-107° at 1.5 mm; n_D^{20} 1.5270) were prepared by the method described previously [6]. 2-Methyl-2-cyclopenten-1-one (III) (b.p. 52-53° at 15 mm; n_D^{20} 1.4770) and 2-cyclopenten-1-one (XI) (m.p. 45° at 15 mm; n_D^{20} 1.4700) were prepared by the method developed in our laboratory [7]. 3,5-Dimethyl-3-cyclopentene-1,2-dione (XIII) (m.p. 66-67°) was prepared by the oxidation of 2,4-dimethyl-2-cyclopenten-1-one with selenium. dioxide [8].

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-Methyl-2-cyclopenten-1-one (III)

A mixture of 6.9 g of the dienone I and 13.8 g of freshly distilled 2-methyl-2-cyclopenten-1-one (III) was heated in a carbon dioxide atmosphere in a sealed glass tube at 150° for six hours. The excess of ketone (11.4 g) was distilled off in a water bath, at first at 15 mm, and towards the end at 2 mm. The viscous residue (8.2 g) was mixed with 7 ml of petroleum ether and set aside to crystallize. After five hours the first crop of crystals was separated (1.3 g; m.p. 117-120°). On the next day two further crops of crystals were separated from the mother liquor (0.65 g, m.p. 103-108°; 0.2 g. m.p. 125-141°).

Several such experiments were performed, and from a total amount of 22.4 g of the dienone I, 6.9 g of a crystalline mixture of isomers of 10,14-dimethyl-9-cardosterene-3,15-dione (IV A, IV B, and IV C) was obtained. Vacuum distillation of the mother liquor yielded 7.2 g of the original dienone (I) and 5 g of a noncrystallizing oil, b.p. 160-170° at 0.5 mm. The yield of the crystalline mixture of isomers was therefore 20% on the total amount of the dienone I taken, and 30% on the amount that reacted.

By fractional crystallization of the first and second crops of crystals, 2.75 g of the isomer IV A, m.p. 131-133°, was isolated. The third crop yielded 0.35 g of the isomer IV B, m.p. 155-156°. After the mother liquors from the isolation of the isomer IV A had stood for three months, crystals of the isomer IV C, m.p. 127-128°, were separated (0.2 g).

Isomer IV A, irregular prisms, m.p. 131-133°.

		Found %: C 79.4; 79.5; H 9.3; 9.1
$C_{19}H_{26}O_2$	Calculated %:	C 79.7; H 9.1

Isomer IV B, irregular prisms, m.p. 155-156°.

		Found %: C 79.8; 79.8; H 9.3; 9.25
$C_{19}H_{26}O_2$	Calculated %:	C 79.7; H 9.1

Isomer IV C, m.p. 127-128°.

		Found %: C 78.2; 78.2; H 9.0; 9.1
$C_{19}H_{26}O_2$	Calculated %:	C 79.7; H 9.1

Isomerization of the Diketone IV A

A mixture of 225 mg of the diketone IV A, m.p. 131-132°, 5 ml of acetic acid, 5 ml of concentrated hydrochloric acid, and 6 ml of toluene was boiled under reflux for nine hours. The toluene layer was separated, neutralized, by agitation with a 4% solution of caustic soda, and filtered. The solvent was removed under reduced pressure, and the solid residue was crystallized from 1 ml of alcohol, yielding 195 mg of 10,14-dimethyl-8-cardosterene-3,15-dione (IV D), m.p. 97-100°. Recrystallization from petroleum ether gave a pure product of m.p. 100-100.5°.

		Found %: C 79.5; 79.6; H 9.0; 9.2
$C_{19}H_{26}O_2$	Calculated %:	C 79.7; H 9.1

Isomerization of the Diketone IV B

The isomerization was performed as above: from 187 mg of the diketone IV B, m.p. 155-156°, after the usual treatment of the reaction mixture and successive crystallizations from petroleum ether and alcohol, 29 mg of the diketone IV E, m.p. 91-93°, was obtained.

$$\begin{array}{lll} & \text{Found \%:} & \text{C 79.65; 79.7; H 9.3; 9.0} \\ C_{19}H_{26}O_2 & \text{Calculated \%:} & \text{C 79.7; \quad H 9.1} \end{array}$$

In admixture with the diketone IV D it showed a strong depression in melting point (melted at 80-85°).

Clemmensen Reduction of the Diketone IV A

A mixture of 1 g of the diketone IV A, m.p. 131-133°, 17 ml of acetic acid, 17 ml of concentrated hydrochloric acid, 17 ml of toluene, and 6.5 g of amalgamated zinc was boiled under reflux for seven hours. The toluene layer was separated, neutralized by agitation with a 5% solution of caustic soda, and filtered. The solvent was removed under reduced pressure, and the noncrystallizing residue was dissolved in 2 ml of petroleum ether and set aside to crystallize at −70°. The precipitated crystals were washed twice by decantation with petroleum ether, and were dried in a desiccator. The product was 0.35 g of 10,14-dimethyl-8-cardosteren-15-one (V) in the form of white, poorly defined crystals, m.p. 53-54°.

$$\begin{array}{lll} & \text{Found \%:} & \text{C 84.3; 84.2; H 10.5; 10.4} \\ C_{19}H_{28}O & \text{Calculated \%:} & \text{C 83.8; \quad H 10.3} \end{array}$$

The dinitrophenylhydrazone formed orange needles, m.p. 193-194° (corr.).

Clemmensen Reduction of the Diketone IV B

The reduction was performed as above: from 300 mg of the diketone IV B, m.p. 155-156°, 80 mg of the ketone VI, m.p. 88-91°, was isolated. Crystallization from 1 ml of petroleum ether (at −70°) gave 55 mg of pure ketone VI, m.p. 94-95°.

$$\begin{array}{lll} & \text{Found \%:} & \text{C 83.3; 83.3; H 10.15; 10.15} \\ C_{19}H_{30}O & \text{Calculated \%:} & \text{C 83.8; \quad H 10.3} \end{array}$$

The dinitrophenylhydrazone formed orange needles, m.p. 191-193°.

Dehydrogenation of the Ketone V

A mixture of 2.5 g of the ketone V, 3.3 g of palladized charcoal (10% Pd), and 30 ml of dry benzene was heated in a nitrogen atmosphere (initial pressure 25 atm) in a rotating autoclave at 350° for six hours. The reaction mixture was filtered, and benzene was removed from the filtrate at a moderately low pressure. The residue partially crystallized out at −70°, yielding 0.4 g of crystals, m.p. 76-86°. Crystallization from petroleum ether yielded 0.2 g of 2-ethyl-1-methylphenanthrene (VII), m.p. 100-102°. In admixture with a previously prepared sample of 2-ethyl-1-methylphenanthrene [1] there was no depression of melting point.

$$\begin{array}{lll} & \text{Found \%:} & \text{C 92.8; H 7.1} \\ C_{17}H_{16} & \text{Calculated \%:} & \text{C 92.7; H 7.3} \end{array}$$

The hydrocarbon was somewhat contaminated with high-melting substances, and this had an effect on the subsequent oxidation of the quinone VIII, the yield of which was low (4 mg of the quinone was obtained from 20 mg of the hydrocarbon). The quinoxaline IX, prepared from the quinone, melted at 110-111°, and showed no depression in admixture with an authentic sample [1].

Dehydrogenation of the Ketone VI

The dehydrogenation was performed as in the preceding experiment, 1.5 g of the ketone VI being used. After filtration and removal of benzene, a yellow oil remained, which did not crystallize even at −70°. It was dissolved in 10 ml of petroleum ether and chromatographed on 10 g of aluminum oxide.

Fraction I, 5 ml of petroleum ether;	213 mg, colorless oil
Fraction II,	157 mg, yellow oil
Fraction III,	87 mg, crystals, impregnated with oil
Fraction IV, V, each 5 ml of petroleum ether;	72 mg, crystals, impregnated with oil
Fraction VI, VII, VIII,	58 mg, oil

Further elutions with mixtures of petroleum ether and benzene, and also with ether and with alcohol, gave only liquid fractions. Crystallization of fractions III-V from petroleum ether at −70° yielded 23 mg of the hydrocarbon VII, m.p. 94-96°. In admixture with known 2-ethyl-1-methylphenanthrene there was no depression of melting point.

Condensation of 3,4,4a,5,6,8a-Hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-Methyl-2-cyclopenten-1-one (III)

A mixture of 4.9 g of the dienone II and 10.9 g of freshly distilled 2-methyl-2-cyclopenten-1-one (III) was heated in a sealed glass tube for six hours at 150°. After removal of the excess of ketone (7.0 g) under a residual pressure of 15 mm in a water bath, the residue began to crystallize out. Alcohol (3 ml) was added, and after two hours the precipitated crystals (2.0 g, m.p. 169-170°) were filtered off at the pump. The mother liquor was evaporated down, and residual methylcyclopentenone (1 g) was removed at a residual pressure of 1 mm. The residue was dissolved in a mixture of 4 ml of petroleum ether and 1 ml of benzene and was set aside for one day. A second crop of crystals (0.7 g, m.p. 160-170°) came down. The second mother liquor, after three days' standing, yielded a third crop of crystals (0.15 g, m.p. 170-180°). The total yield of a crystalline mixture of isomers of 10,14-dimethyl-9-cardosterene-2,15-dione (X A, X B, and X C) was 2.85 g (38% on the amount of dienone II taken).

By fractional crystallization from alcohol of the first and second crops of crystals, in conjunction with mechanical separation of crystals, the following isomers were obtained: X A, m.p. 184-185°, 1.45 g, and X B, m.p. 154-154.5°, 0.42 g. Crystallization of the third crop yielded the isomer X C, m.p. 192-193°, 60 mg.

Isomer X A, m.p. 184-185° (corr.).

	Found %:	C 79.9; 79.9; H 9.2; 9.2
$C_{19}H_{26}O_2$	Calculated %:	C 79.7; H 9.1

Isomer X B, m.p. 154-154.5°.

	Found %:	C 79.6; H 9.1
$C_{19}H_{26}O_2$	Calculated %:	C 79.7; H 9.1

Isomer X C, m.p. 192-193° (corr.).

	Found %:	C 79.6; 79.55; H 9.2; 9.1
$C_{19}H_{26}O_2$	Calculated %:	C 79.7; H 9.1

A mixture of the isomers X A and X C melted at 160-170°.

Isomerization of the Diketone X A

A mixture of 200 mg of the diketone X A, m.p. 184-185°, 6 ml of acetic acid, 10 ml of hydrochloric acid, and 6 ml of toluene was boiled under reflux for four hours. The toluene layer was separated, neutralized by agitation with a 5% solution of caustic potash, and filtered. The solvent was removed under moderately low pressure, and the crystalline residue was recrystallized from 1.5 ml of alcohol, yielding 50 mg of the original diketone X A, m.p. 182-183°. Slow evaporation of solvent from the mother liquor yielded a mixture of the diketones X A and X D, which were separated mechanically. In this way, 16 mg of 10,14-dimethyl-8-cardosterene-2,15-dione (X D) was obtained in the form of white prisms, m.p. 124-125°.

	Found %:	C 80.0; 79.7; H 9.0; 9.15
$C_{19}H_{26}O_2$	Calculated %:	C 79.7; H 9.1

Clemmensen Reduction of the Diketone X A

A mixture of 800 mg of the diketone X A, m.p. 184-185°, 10 ml of acetic acid, 15 ml of hydrochloric acid, 6 ml of toluene, and 4 g of amalgamated zinc was boiled under reflux for 3 hours 30 minutes. The toluene layer was separated and neutralized, and the toluene was removed under reduced pressure. The residue was crystallized at −70° from petroleum ether, yielding 50 mg of the ketone VI, m.p. 83-86°. Recrystallization from petroleum ether raised the melting point to 89-91°. A mixture melting point with the sample of VI described above gave no depression. The dinitrophenylhydrazone melted at 192-194°, and this also gave no depression in admixture with the dinitrophenylhydrazone of VI described above.

Clemmensen Reduction of the Diketone X B

The reduction was performed as in the preceding experiment: from 300 mg of the diketone X B, m.p. 154-154.5°, 20 mg of the ketone V, m.p. 49-51°, was obtained. A mixture melting point with the above-described

sample of this ketone showed no depression. The dinitrophenylhydrazone melted at 191-193°, and this also gave no depression in admixture with the previous sample.

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-Cyclopenten-1-one (XI)

A mixture of 2.5 g of the dienone I and 5.7 g of freshly distilled 2-cyclopenten-1-one (XI) was heated in a carbon dioxide atmosphere in a sealed glass tube at 130° for 11 hours. The cyclopentenone that had not reacted (4.1 g) was distilled off at 15 mm, and the residue partially crystallized out when 5 ml of petroleum ether was added, yielding 0.4 g (11%) of a crystalline mixture of isomers (XII A and XII B) of 10-methyl-9-cardosterene-3,15-dione, m.p. 118-125°. Two recrystallizations of the mixture from petroleum ether-benzene (3 : 1) yielded 100 mg of the isomer XII A, m.p. 123-124°.

$$\text{C}_{18}\text{H}_{24}\text{O}_2;\quad \begin{array}{l}\text{Found \%:} \quad \text{C 79.2; 79.2; H 8.9; 9.1}\\ \text{Calculated \%:}\quad \text{C 79.4;} \qquad \text{H 8.9}\end{array}$$

From the mother liquor, after removal of unchanged dienone I (0.5 g), 80 mg of crystals, m.p. 155-150°, were separated in the usual way. Two recrystallizations from a mixture of petroleum ether and benzene (3 : 1) yielded 20 mg of the isomer XII B, m.p. 156-157°.

$$\text{C}_{18}\text{H}_{24}\text{O}_2;\quad \begin{array}{l}\text{Found \%:} \quad \text{C 79.4; 79.7; H 8.8; 9.0}\\ \text{Calculated \%:}\quad \text{C 79.4;} \qquad \text{H 8.9}\end{array}$$

Condensation of the dienone I with the cyclopentenone XI at 160° was accompanied by much resinification, and the yield of crystalline products was reduced by a factor of two.

Condensation of 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 3,5-Dimethyl-3-cyclopentene-1,2-dione (XIII)

A solution of 1.1 g of the dienone I and 0.6 g of the diketone XIII in 3 ml of absolute benzene was heated in a carbon dioxide atmosphere in a sealed glass tube at 100° for six hours. The benzene was removed under reduced pressure, and the residue was diluted with 5 ml of ether and set aside to crystallize at −10°. After four days a considerable amount of crystals had formed, and these were recrystallized from alcohol, yielding 140 mg of the tetracyclic triketone XIV in the form of yellow needles, these show incipient melting at 108-110°, solidify again at 112-115°, and melt again at 167-168°.

$$\text{C}_{20}\text{H}_{26}\text{O}_3.\quad \begin{array}{l}\text{Found \%:} \quad \text{C 76.1; 76.3; H 8.3; 8.5}\\ \text{Calculated \%:}\quad \text{C 76.4;} \qquad \text{H 8.3}\end{array}$$

The mother liquor was dissolved in petroleum ether and chromatographed on aluminum oxide. Elution with benzene yielded 100 mg of the tetracyclic diketo enol XV in the form of colorless, well-formed crystals, m.p. 167-168°. An alcoholic solution of the substance gave a violet color with an aqueous-alcoholic solution of ferric chlorides.

$$\text{C}_{20}\text{H}_{26}\text{O}_3.\quad \begin{array}{l}\text{Found \%:} \quad \text{C 76.4; 76.6; H 8.3; 8.3}\\ \text{Calculated \%:}\quad \text{C 76.4;} \qquad \text{H 8.3}\end{array}$$

Isomerization of the Triketone XIV

One drop of piperidine was added to a solution of 70 mg of the triketone XIV, m.p. 108-110°, in 1.5 ml of dioxane. The solution became clear after 15 minutes' standing, and 0.5 ml of water was then added, the turbidity that appeared being removed by addition of a drop of alcohol. Colorless crystals soon began to appear, and 60 mg of the diketo enol XV, m.p. 167-168°, was obtained. A mixture melting test with the above-described sample gave no depression. When the condensation of the dienone I with the diketone XIII was carried out at 120°, it was not found possible to isolate any of the triketone XIV, only the diketo enol XV being obtained.

Condensation of 3a,4,7,7a-Tetrahydro-3,7a-dimethyl-1-indanone with Diethyl Oxalate.

3a,4,7,7a-Tetrahydro-3,7a-dimethyl-1-indanone was prepared by the condensation of 1,3-butadiene with 2,4-dimethyl-2-cyclopenten-1-one [9], and had b.p. 90-92° at 7 mm, n_D^{20} 1.4875. Ground sodium ethoxide (11 g, prepared from 3.7 g of sodium) was placed in a three-necked flask fitted with reflux condenser, and dropping funnel. The flask was filled with nitrogen, and a solution of 19.5 g of diethyl oxalate in 80 ml of benzene was added. The

mixture was heated in a water bath for 10 minutes, and the sodium ethoxide went completely into solution. The solution, which had become dark in color, was cooled to 20° and was stirred while a solution of 14.8 g of 3a,4,7,-7a-tetrahydro-6,7a-dimethyl-1-indanone in 40 ml of benzene was added dropwise. Heat was evolved, and the mixture became black. It was set aside for five hours at 20°, and then treated with water. The benzene layer was neutralized by agitation with dilute hydrochloric acid, the solvent was driven off, and the residue was vacuum-distilled, yielding 11.2 g of the condensation product, b.p. 142-143° at 1 mm, n_D^{20} 1.5070.

$$\text{Found \%:} \quad C\ 68.2;\ 68.3.\ H\ 7.6;\ 7.6$$

$C_{15}H_{22}O_4$.   Calculated %: C 68.15;   H 7.6

Attempts at eliminating carbon monoxide from this product by heating with glass and iron powder at 180-200° were without result: the substance was recovered unchanged, apart from some resinification.

SUMMARY

1. Total syntheses of the steroid diketones IV and X of the cis-cis series have been effected by condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) and 3,4,4a,5,6,6a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (II) with 2-methyl-2-cyclopenten-1-one (III). From the mixtures of isomers formed (IV and X), in each case three isomeric diketones were isolated, two of which, i.e., those formed in the greatest amount, have been shown to have "inverted" structures and to differ with respect to the spatial arrangement of substituents at $C_{13}-C_{14}$.

2. 3,4,4a,7,8,8a-Hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) has been condensed also with 2-cyclopenten-1-one (XII), and two isomeric steroid diketones (XI) have been isolated.

3. Condensation of the hexahydromethylvinyl-2(1H)-naphthalenone I with 3,5-dimethyl-3-cyclopentene-1,2-dione (XIII) yielded the steroid triketone XIV, which very readily isomerizes into the diketo enol XV.

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*****See Consultants Bureau Translation, page 787.
******See Consultants Bureau Translation, page a-211.
*******See Consultants Bureau Translation, page 911.

SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

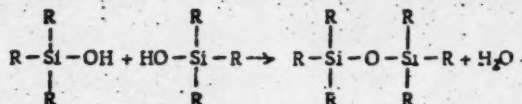## COMMUNICATION 1. SYNTHESIS OF ORGANOSILICON ACETALS

M. F. Shostakovsky, I. A. Shikhiev, and D. A. Kochkin

Oxygen-containing organosilicon compounds, such as silanols of general formula

$$\begin{array}{c} R \\ R - SiOH \\ R \end{array}$$

(R = alkyl or aryl), are of great theoretical interest. There are great prospects for development in organic chemistry along the line of the unification of organic and organosilicon syntheses. The authors of this paper have undertaken the task of working out new syntheses of organosilicon compounds.
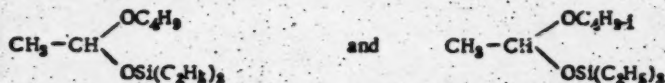
It has been shown by the work of Andrianov [1] and others [2] that organosilicon compounds have certain peculiar properties. It is well known, for example, that tertiary alcohols are readily dehydrated to unsaturated hydrocarbons, whereas trialkylsilanols, on dehydration, give stable siloxane dimers:

$$\begin{array}{ccccc} R & & R & & R \quad R \\ | & & | & & | \quad | \\ R-Si-OH + HO-Si-R \rightarrow & R-Si-O-Si-R + H_2O \\ | & & | & & | \quad | \\ R & & R & & R \quad R \end{array}$$
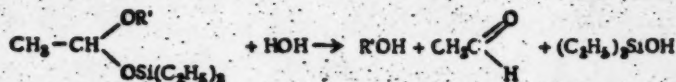
We now describe a new synthesis of oxygen-containing organosilicon compounds based on the reaction of vinyl ethers with silanols. In the course of this work we have established that the reaction of alkyl vinyl ethers with trialkylsilanols proceeds similarly to the corresponding reaction with organic tertiary alcohols and may be represented by the equation:

$$R_3SiOH + CH_2 = CHOR' \rightarrow CH_3 - CH \underset{OSi(R)_3}{\overset{OR'}{<}}$$
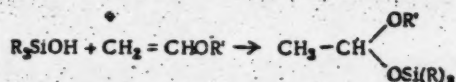
We have studied methods for the preparation of the following acetals:

$$CH_3 - CH \underset{OSi(C_2H_5)_3}{\overset{OC_4H_9}{<}} \quad \text{and} \quad CH_3 - CH \underset{OSi(C_2H_5)_3}{\overset{OC_4H_9-i}{<}}$$
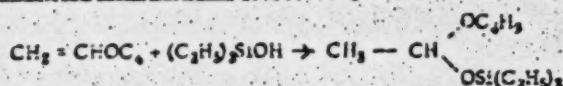
Addition of trialkylsilanols to vinyl ethers proceeds fairly readily in presence of traces of 30% hydrochloric acid, the procedure being that which has been developed for the synthesis of acetals of organic alcohols [3]. We have in this way prepared and characterized two unsymmetrical acetals: the butyl triethylsilyl and the isobutyl triethylsilyl acetals of acetaldehyde. The structures of the organosilicon acetals obtained were proved by the products of their hydrolysis, which proceeds according to the equation:

$$CH_3 - CH \underset{OSi(C_2H_5)_3}{\overset{OR'}{<}} + HOH \rightarrow R'OH + CH_3C \underset{H}{\overset{O}{<}} + (C_2H_5)_3SiOH$$

1. Synthesis of Acetaldehyde Butyl ...

$$CH_2 = CHOC_4 + (C_2H_5)_3SiOH \rightarrow CH_3 - CH \begin{matrix} OC_4H_9 \\ OSi(C_2H_5)_3 \end{matrix}$$

To a cold (room temperature) mixture of 33 g (0.25 mole) of triethylsilanol (b p 80°/30 mm; d_4^{26} 0.8652; n_D^{20} 1.4332) and 25 g (0.25 mole) of butyl vinyl ether (b.p. 93-94°; d_4^{20} 0.7790; n_D^{20} 1 4020) 0.02 ml of 30% hydrochloric acid was added, and the temperature rose to 48°. After one hour the contents of the flask were heated under reflux in a water bath at 80-93° for one hour, and they were then set aside overnight. On the next day the reaction mixture was neutralized, and dried with potassium carbonate The potassium carbonate was then filtered off, and the filtrate was distilled at atmospheric pressure, the following fractions being obtained:
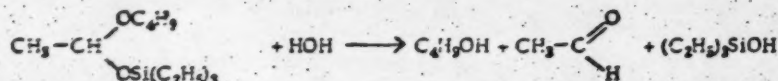
Fraction   I, b.p. up to 213°; 8g
Fraction   II, b.p. 214-216°; 14 g; n_D^{20} 1.4258
Fraction   III, b.p. 217-218°; 22 g; n_D^{20} 1.4274
Residue 4 g

Fractions II and III were united and refractionated, yielding 32 g of a product boiling at 82-83°/9 mm; yield 55 17% on the amount of butyl vinyl ether taken. This substance had the following constants: d_4^{20} 0.8574; n_D^{20} 1.4271; found MR 69.49; calculated for $C_{12}H_{28}SiO_2$ MR 69.85.

Found %: C 62.49; 62 60, Si 11.74; 11.88; H 12.20, 12.25
$C_{12}H_{28}SiO_2$ Calculated %: C 62.06;   Si 12.09;   H 12.07

From the results obtained it follows that the substance of b.p. 82-83°/9 mm was acetaldehyde butyl triethylsilyl acetal. It was a clear oily liquid having an ethereal odor; it did not change in storage.

2. Hydrolysis of the Butyl Triethylsilyl Acetal

$$CH_3-CH \begin{matrix} OC_4H_9 \\ OSi(C_2H_5)_3 \end{matrix} + HOH \longrightarrow C_4H_9OH + CH_3-C \begin{matrix} O \\ H \end{matrix} + (C_2H_5)_3SiOH$$

Acetaldehyde was estimated in the products of the hydrolysis of the unsymmetrical organosilicon acetal by the bisulfite method. It was found that hydrolysis of the acetal by treatment with 2% sulfuric acid at 60° for 12 hours did not go well, and in further work the hydrolysis was carried out in a boiling water bath in presence of 5% sulfuric acid.

The acetal (0.3213 g) was heated with 50 ml of 5% sulfuric acid in a sealed tube for six hours. The contents of the tube were then transferred to a 200-ml measuring flask and made up to volume with distilled water. Analysis by the bisulfite method gave 86.39% of acetaldehyde (of the theoretical amount) A parallel experiment by the same method (0.4391 g of acetal) gave 84.28% of acetaldehyde. Towards the end of the hydrolysis process, an oily layer formed on the surface of the solution; this was evidently one of the hydrolysis products. The hydrolysis results show that the substance of b.p. 82-83°/9 mm was the butyl triethylsilyl acetal. It should be noted that the described hydrolysis conditions do not yield quantitative results.

3. Synthesis of Acetaldehyde Isobutyl Triethylsilyl Acetal

$$CH_2 = CHOC_4H_9-i + (C_2H_5)_3SiOH \rightarrow CH_3CH \begin{matrix} OC_4H_9 \ (-i) \\ OSi(C_2H_5)_3 \end{matrix}$$
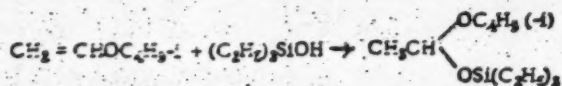
The conditions of the synthesis were similar to those of the preceding experiment. A mixture of 33 g (0.25 mole) of triethylsilanol and 25 g (0.25 mole) of isobutyl vinyl ether (b.p. 83°; n_D^{20} 1.3986; d_4^{20} 0.7680) was placed   in a 150-ml round-bottomed flask fitted with reflux condenser, thermometer, and mechanical stirrer. The mixture was constantly stirred at room temperature, and 0.02 ml of 30% hydrochloric acid was added, when the temperature rose to 45°. Stirring was continued for 90 minutes, and the temperature was raised to 84°. The mixture was set aside overnight, and on the next day it was dried with calcined potassium carbonate, and distilled, the following fractions being obtained:

Fraction I, b.p. up to 209°;   13 g
Fraction II, b.p 210-215°;   38 g
Residue   4 g

Fraction II was refractionated, and yielded 30 g (51.72% on the amount of isobutyl vinyl ether taken) of a product of b.p. 75-76°/ 7 mm.

It must be pointed out that after each distillation there remained some liquid at the bottom of the flask which was not distillable under the conditions indicated: at a higher temperature it decomposed. The constants of the product of b.p. 75-76°/ 7 mm were d_4^{20} 0.8530; n_D^{20} 1.4252; found MR 69.58; calculated for $C_{12}H_{28}SiO_2$ MR 69.85.

Found %: C 62.14; 61.97; Si 12.31; 12.10; H 12.70; 12.48
$C_{12}H_{28}SiO_2$. Calculated %: C 62.06; Si 12.09; H 12.07

From these results it will be seen that the product of b.p. 75-76°/ 7 mm was acetaldehyde isobutyl triethyl-silyl acetal. It was a clear oily liquid having an ethereal odor.

In conclusion it must be pointed out that organosilicon acetals are comparatively stable substances. The butyl triethylsilyl acetal is evidently more stable than the isobutyl compound.

SUMMARY

1. It has been shown, for the first time, that triethylsilanol condenses with butyl vinyl and isobutyl vinyl ethers under conditions similar to those required in the corresponding syntheses with organic alcohols.

2. Two unsymmetrical organosilicon acetals of acetaldehyde, the butyl triethylsilyl and isobutyl triethyl-silyl acetals, have been synthesized and described for the first time.

3. The proposed method is a general one for the preparation of various organosilicon acetals from alkyl vinyl ethers and trialkylsilanols.

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EFFECT OF COMPRESSION ON THE POROSITY, CATALYTIC PROPERTIES, AND CHROMATOGRAPHIC ACTIVITY OF SILICA GEL

L. Kh. Freidlin, L. F. Vereshchagir, I. E. Neimark,
I. U. Numanov, and R. Yu. Sheinfain

As we have previously shown [1, 2], the porosity characteristics of silica gel greatly influence its activity and selectivity in the vapor-phase hydrolysis of chlorobenzene. When in addition to a large volume of fine pores the silica gel has a sufficiently large volume of connective pores through which the reactants and products can be transported to active centers, it forms a catalyst upon which diffusional retardation is not observed. When, on the contrary, the volume of connective pores is insufficiently large and the internal surface is not readily accessible, diffusional retardation of the process is to be observed. It is natural to suppose that, if we apply a high pressure to the silica gel, its specific surface and porosity characteristics will alter, and, at the same time, its adsorption and catalytic properties will also alter.

EXPERIMENTAL

Variation in the Porosity Characteristics of Silica Gels Compressed at Various Pressures.

The samples of silica gels were compressed in copper ampoules, 50 mm in length, 10 mm in external diameter, and 9.6 mm in internal diameter. In order to distribute the pressure evenly over the whole of the ampoule, the latter was wrapped in lead foil. Finely ground silica gel was rammed tightly into the ampoule, which was then closed and subjected to pressure in the multiplier described previously [3].

Structural Characteristics of Samples of Silica Gel Before and After Compression at Various Pressures

Figures 1 and 2 show the sorption isotherms for methanol vapor on silica gel, before and after compression. It will be seen from Table 1 that the reduction in the limiting sorptive capacity of the pores resulting from an increase in compression from zero to 5000 atm was considerably greater for the sample having the larger pores. For this sample the further reduction in sorptive capacity due to increase in compression from 5000 to 10,000 atm was much less, and there was practically no further reduction when the compression was increased to 20,000 atm. The greatest reduction for the coarse sample occurred, therefore, in the 0-5000 atm range, whereas it will be seen that, for finely porous silica gel, the greatest reduction occurred in the 5000-10,000 atm range. Reduction of the limiting sorptive capacity of the pores by means of compression was therefore effected more readily for the coarse silica gel, which had the greatest volume of connective pores. Although the limiting sorptive capacity of the pores of the coarsely porous sample was greatly reduced by increase in compression from zero to 5000 atm, there was no corresponding change in specific surface; whereas, in the 10,000-20,000 atm range, in which there was only a small fall in the limiting sorptive capacity, there was an appreciable reduction in specific surface. Mechanical action, therefore, leads mainly to the destruction of connective pores, whereas thermal action leads mainly to the destruction of the fine pores [2].

Table 1 shows also that, although the limiting sorptive capacity of the pores of the coarsely porous sample was 0.80 ml/g, and that of the finely porous silica gel only 0.34 ml/g, compression at 10,000 atm resulted in a leveling out of the limiting sorptive capacities of the two samples, which were reduced to 0.19-0.21 ml/g and were not appreciably reduced further when the pressure was raised to 20,000 atm. The limit of compression of the silica gel was evidently already attained at 10,000 atm. The sorption isotherm for silica gel compressed at 5000 atm shows considerable hysteresis, i.e. a part of the connective pores were preserved (Fig. 2, Curve 1). On the other hand, the sorption isotherms for the samples compressed at 10,000 and 20,000 atm show very little hysteresis and are almost coincident (Figs. 1 and 2, Curve 2). At such pressures, therefore, the connective pores were almost completely destroyed.

TABLE 1

Structural Characteristics of Eight Samples of Silica Gel (Not Compressed, and Compressed at Various Pressures)

Sample of silica gel	Coarsely porous				Finely porous			
	not com- pressed	compressed at			not com- pressed	compressed at		
		5000 atm	10000 atm	20000 atm		5000 atm	10000 atm	20000 atm
Limiting sorptive capacity of the pores (sum of volumes of micro and connective pores) (ml/g)	0.80	0.38	0.21	0.19	0.34	0.29	0.19	0.19
Specific surface (sq.m/g)	350	350	310	260	680	–	290	290
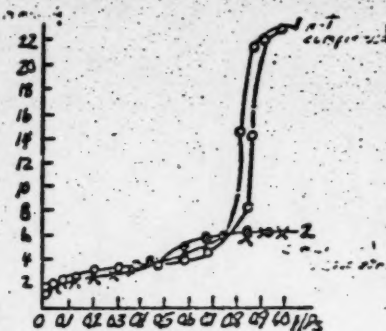
Fig. 1. Adsorption isotherms for methanol vapor on coarsely porous silica gel: 1) not compressed; 2) compressed at 10,000 atm.
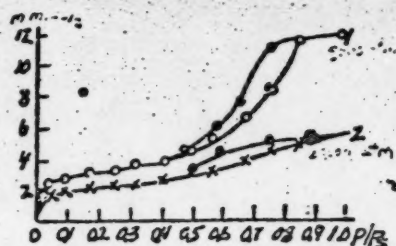

Fig. 2. Adsorption isotherms for methanol vapor on coarsely porous silica gel: 1) compressed at 5000 atm, 2) compressed at 20,000 atm

Conditions of the Catalytic Experiments, and the Analytical Method

The reaction was carried out in a continuous-flow system. Water and chlorobenzene were supplied from two automatically regulated burets [4], and passed to a quartz flask at 250°, which served as a superheater, and then from the side tube of the flask to the reaction tube containing the catalyst. The water-chlorobenzene ratio was close to unity in all experiments. The volume of catalyst was 10 ml. Each experiment lasted 90 minutes, and in the course of this time 4 ml of chlorobenzene and 5 ml of water were passed. All the silica gel samples were promoted by cupric chloride (2%). Regeneration of the catalyst was effected by a two-hour treatment with air at 500°, following experiments at 500, 550, and 600°. The reaction products were analyzed for phenol and hydrochloric acid.

Comparative Activity, Productivity, and Specificity of Samples of Silica Gel Compressed at Various Pressures

It will be seen from Figures 3 and 4 that the activity per unit volume, i.e. the productivity, of coarsely porous silica gel depends on the reaction temperature and on the pressure at which the silica gel was compressed. The productivity of the sample compressed at 5000 atm was higher than that of the uncompressed sample at all temperatures from 400° to 550°. The productivity of the sample compressed at 10,000 atm was about equal
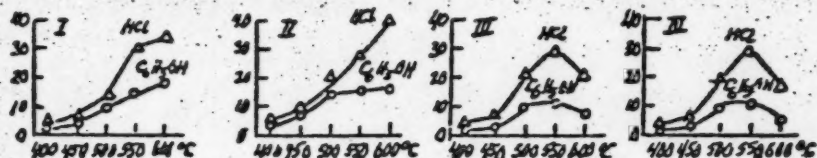

Fig. 3. Hydrolysis of chlorobenzene in presence of samples of coarsely porous silica gel (not compressed, and compressed at various pressures): I) not compressed; II) compressed at 5000 atm; III) compressed at 10,000 atm; IV) compressed at 20,000 atm

to, and the one compressed at 20,000 atm somewhat lower than, the original uncompressed sample. The specific volume of the silica gel was reduced by a factor of about 1.5 by compression at 20,000 atm, so that its specific activity (i.e., activity per unit weight) was lower than that of the uncompressed material.

For the finely porous silica gel, the rise in productivity due to compression at 500 atm was less, and the fall in specific activity was still greater than before (Figs. 5 and 6). The effect of compression at 20,000 atm was particularly great for the finely porous silica gel S-1. Not only the specific activity, but also the productivity, of this catalyst was lower after compression (Table 2.).

The selectivity of samples compressed at 5000 atm was very little different from that of the uncompressed samples, and the selectivity of samples compressed at 10,000 and 20,000 atm was lower than that of the uncompressed sample (Figs. 7 and 8). The greater the compression employed, the lower the temperature at which side processes made their appearance. The higher the temperature, the greater the importance assumed by the side processes on the compressed samples of silica gel and the higher the yield of acid as compared with that of phenol.

The results are completely in agreement with the changes in density and porosity characteristics occurring during compression. On the one hand, increase in pressure results in an increase in the density of the sample, and for this reason the productivity of a sample compressed at 5000 atm is greater than that of the original sample. On the other hand, the higher the pressure under which the silica gel is compressed, the more inaccessible does its active surface become, the more rapidly does it become carbonized, and the more prominent do the side processes become. For this reason, the productivity of a sample compressed at 20,000 atm is less than that of the uncompressed sample.
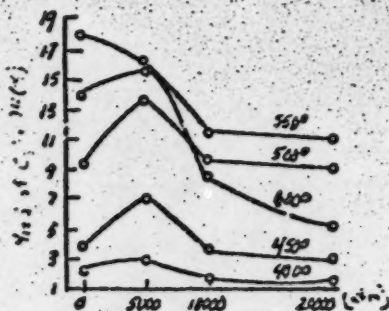

Fig. 4. Yield of phenol in presence of samples of coarsely porous silica gel (not compressed, and compressed at various pressures).

TABLE 2
Productivity and Specificity of Uncompressed and Compressed Samples of Silica Gel S-1

	Not compressed				Compressed		
Tempera-ture (°C)	Yield (%)		HCl	Tempera-ture (°C)	Yield (%)		HCl
	C_6H_5OH	HCl	C_6H_5OH		C_6H_5OH	HCl	C_6H_5OH
450	7.3	8.1	1.1	400	2.9	4.0	1.4
500	15.7	16.2	1.0	450	6.2	8.9	1.5
550	29.1	31.4	1.1	500	8.4	11.6	1.4
600	36.6	42.9	1.1	550	16.1	21.9	1.4
650	38.4	53.0	1.4	600	21.0	31.8	1.5

Effect of Compression on the Chromatographic Activity of Silica Gel

Ground silica gel was fractionated by passage through sieves, and the 100/200 mesh per sq. in. fraction was separated and dried at 150° for 5-6 hours. The silica gel prepared in this way was rammed tightly into a glass tube, diameter 10 mm and length 500 mm, which was fitted with a jacket (thermostat). A mixture of benzene (10% by volume) and heptane (90% by volume) of refractive index n_D^{20} 1.3980 was prepared, and 20 ml of it was passed through the silica gel column at a rate of about 0.8 ml per minute. The liquid passing through was collected in a receiver, and it was tested periodically for benzene by the formolite reaction. An orange coloration indicated that benzene was beginning to pass and the sorbent was completely saturated.

The chromatographic activity a (ml/g) was calculated by the formula $a = \dfrac{b \cdot c \cdot 100}{m \cdot d}$, where b is the benzene content (% by vol.) of the original mixture; c is the amount (ml) of pure heptane separated in the chromatographic process; d is the heptane content (% by vol.) of the original mixture; and m is the weight (g) of silica gel [5].
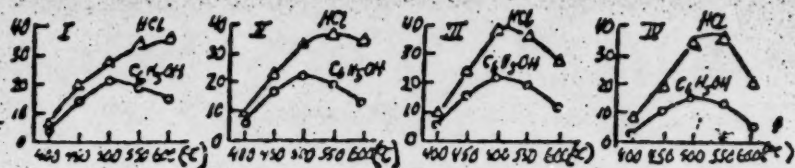
Fig. 5 Hydrolysis of chlorobenzene in presence of samples of finely porous silica gel (not compressed, and compressed at various pressures): I) not compressed; II) compressed at 5000 atm; III) compressed at 10,000 atm; IV) compressed at 20,000 atm
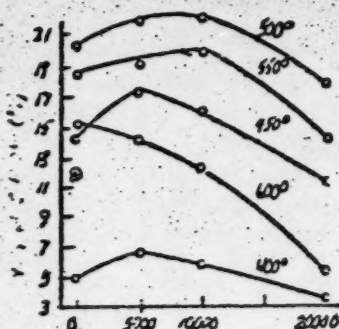

Fig. 6. Yield of phenol in presence of samples of finely porous silica gel (not compressed, and compressed at various pressures)
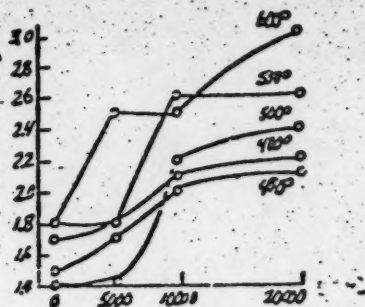
Fig. 7. The ratio of the yields of HCl and C_6H_5OH in presence of samples of coarsely porous silica gel (not compressed, and compressed at various pressures)

TABLE 3
Chromatographic Activity of the Original Silica Gel (10 g)

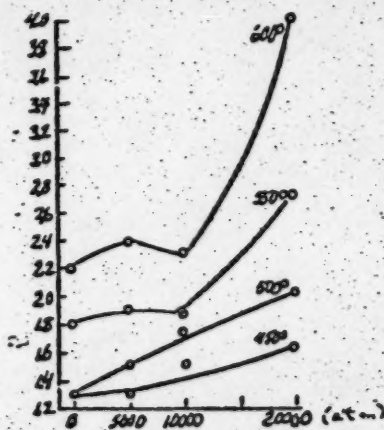| Time (min.)	Temp. of water jacket (°C)	Vol. of pure heptane obtained (ml)	Rate of efflux of heptane (drops/sec)	No. of drops of liquid until positive test with formaldehyde obtained
3	+2	1.0	3.4	−2
11	+2	3.0	4.0	−1
19	+2	5.0	4.0	−1
29	+2	7.0	4.0	−2
39	+2	8.4	4.0	+2
Total 39	Mean +2	Total 8.7	Mean 4.0	Total 6

Fig. 8. The ratio of the yields of HCl and C_6H_5OH in presence of samples of finely porous silica gel (not compressed, and compressed at various pressures).

Six drops, i.e., 0.3 ml of liquid, were tested before a positive reaction with formaldehyde were obtained. Altogether, therefore, 8.7 ml of pure heptane was separated chromatographically: the chromatographic activity of the uncompressed sample of silica gel was 9.7 ml/g (Tables 3 and 4). The chromatographic activity of silica gel compressed at 20,000 atm was 7.3 ml/g, i.e., was about 25% less than its activity in the uncompressed state. No doubt the explanation of this behavior is that the compression process alters the porosity characteristics and specific surface of the silica gel.

TABLE 4

Chromatographic Activity of Silica Gel Compressed at 20,000 atm (11.7 g)

Time (min.)	Temp. of water jacket (°C)	Vol. of pure heptane obtained (ml)	Rate of efflux of heptane (drops/sec)	No. of drops of liquid until positive test with formaldehyde obtained
10	+2	2.0	4.0	−2
20	+2	4.0	4.0	−2
30	+2	6.0	4.0	−2
36	+2	7.1	4.0	+2
Total 36	Mean +2	Total 7.4	Mean 4.0	Total 6

SUMMARY

1. An investigation has been made of the effect of pressures of up to 20,000 atm on the porosity character-istics, adsorption activity, and catalytic properties of silica gel.

2. It has been shown that the greatest reduction (by 50%) in the limiting sorptive capacity of the pores (sum of the capacities of the micro and connective pores of the coarsely porous silica gel) occurs during compression to 5000 atm, but no simultaneous change in specific surface occurs. The greatest reduction in the limiting sorptive capacity of the pores of the finely porous silica gel occurs over the range 5000-10,000 atm. The reduction in the limiting sorptive capacity of the pores is therefore attained by a lower compression for the coarsely porous silica gel. The explanation of this is that the coarsely porous silica gel, unlike the finely porous material, has a greater volume of connective pores. Mechanical action, therefore, primarily destroys the connective pores, whereas ther-mal action destroys the fine pores. In general, the limiting sorptive capacity of the coarsely porous silica gel com-pressed at 5000-10,000 atm does not differ from that of the finely porous material, i.e., the coarsely porous mater-ial is converted by pressure into finely porous material. When the compression is further increased to 20,000 atm, the limiting sorptive capacity of the pores of the samples of finely and coarsely porous silica gels remains practical-ly the same as that of the samples compressed at 10,000 atm.

3. Compression at 20,000 atm results in reduction of the specific surface of coarsely porous silica gel from 350 to 260 sq.m/g. and that of the finely porous silica gel from 680 to 290 sq.m/g. i.e., by 26% and 57% respec-tively.

4. The productivity of samples compressed at 5000 atm is higher, and of those compressed at 20,000 atm lower, than that of the uncompressed sample. The greater the compression, the lower the specific activity.

5. The selectivity of samples compressed at 5000 atm differs little from that of the uncompressed sample, but samples compressed at higher pressures have greatly reduced selectivity. It is possible that samples that have been subjected to higher compression, i.e., have a more severely destroyed porous structure, more readily sinter together, and so become deactivated.

6. It has been shown that the chromatographic activity of silica gel compressed at 20,000 atm is about 25% less than that of the uncompressed sample.

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